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Dredged Material Research Program

TECHNICAL REPORT D-77-25

AN EVALUATION OF OIL AND GREASE CONTAMINATION ASSOCIATED WITH DREDGED MATERIAL CONTAINMENT AREAS

by

Engineering-Science, Inc.
Austin, Texas 78722

November 1977

Final Report

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DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG, MISSISSIPPI 39180

IN REPLY REFER TO: WESYV

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SUBJECT: Transmittal of Technical Report D-77-25

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1. The technical report transmitted herewith represents the result of one of the research efforts initiated in Task 6B (Treatment of Contaminated Dredged Material) of the Corps of Engineers' Dredged Material Research Program (DMRP). This task, included as part of the Disposal Operations Project of the DMRP, is concerned with evaluation of physical, chemical, and/or biological methods for the removal of contaminants from dredged material.

2. In recent years there has been continued concern over the adverse environmental impact of dredging and disposal operations on water quality and aquatic organisms. Rapid industrial and population growth in areas adjacent to navigable waterways has contributed to the contamination of the water bodies and many sediments that are dredged. It became apparent during the planning phases of the DMRP that in some instances it might be necessary, where unacceptable adverse impacts are expected, to treat contaminated dredged material before it could be disposed at designated open-water disposal areas or before the effluent from upland containment areas could be discharged back to the waterways. Therefore, Task 6B was developed to meet this potential need.

3. This study was originally planned to involve three work areas: (a) an appraisal of the magnitude of the problems of oil and grease discharges from dredged material containment areas; (b) the development of a means to predict the appearance of significant levels of oil and grease in return waters; and (c) the evaluation and development of candidate treatment processes for reduction of the oil and grease content of return waters. The study was performed by Engineering Science, Inc., of Austin, Texas.

4. As part of this study, field investigations were conducted at six locations where dredging is practiced in industrialized areas. Both water and sediment samples were collected at these sites and were analyzed for various environmental factors with the intent of establishing whether or not the release of oil and grease from dredged sediment could be

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predicted on the basis of the environmental factors. Results of the field study strongly indicated that oil and grease are not released from sediments to a significant extent during the dredging process. It was found that relatively high oil levels in return waters were associated with high suspended solids concentrations but that the various factors could not be related to the release of oil and grease from sediments.

5. At this point, plans for the remainder of the study were reassessed. It was decided to redirect the efforts of the study to determine the significant environmental factors affecting the release of oil and grease from dredged sediment. Confirmation of the field study results (i.e., that oil and grease were not released from sediment by dredging operations) was another objective of the revised study. Providing that the results of this phase of the study were consistent with previous findings, no further evaluation of treatment methods would be conducted.

6. A series of bench-scale experiments were devised to evaluate the relationship of oil and grease release with several variables (i.e., salinity, pH, temperature, and degree and duration of mixing). The range of conditions evaluated for each of these variables encompassed essentially all conditions likely to occur in the field during dredging operations. The results of the bench-scale study showed no consistent relationship between the various environmental factors and oil and grease release from dredged sediments. The quantity of oil and grease released even under the most severe conditions established by these studies was not appreciably different from levels measured during the field surveys.

7. The overall conclusion of this study is that oil and grease are not released from sediments in significant quantities as a result of dredging. High oil concentrations observed in return waters are associated with high suspended solids concentrations and the oil is sorbed on the solids. Any treatment above and beyond containment to remove suspended solids is not warranted based on the results of this study.

JOHN L. CANNON
Colonel, Corps of Engineers
Commander and Director

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Oils	Water pollution

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The report addresses the potential problem of contamination of receiving waters by oil and grease in return waters from dredged material containment areas. As a part of this study, field studies were conducted at six locations where dredging is practiced, and both water and sediment samples were collected at these sites. The samples were analyzed for various environmental factors with the intent of establishing whether or not the release of oil and grease from dredged sediments could be predicted on the basis of the environmental

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20. ABSTRACT (Continued).

factors. The results of the field study strongly indicated that oil and grease are not released from sediments to a significant extent during the dredging process. It was found that relatively high oil levels in return waters were associated with high suspended solids concentrations, but that the various factors could not be related to the release of oil and grease from sediments. A bench-scale study was devised to delineate the significant factors affecting the release of oil and grease from dredged sediments; however, no consistent relationships were found. The bench-scale results confirmed the field study results in that oil and grease concentrations in the water phase were quite low, even with particularly oily sediments.

The report also presents the following:

a. An evaluation of oil and grease sampling and analytical techniques.

b. A literature review of potential treatment methods for the reduction of the oil and grease contents of containment area return waters.

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EXECUTIVE SUMMARY

The environmental effects of dredging for the maintenance of navigable waterways is a major concern of the Corps of Engineers and regulatory agencies. Contamination of receiving waters by return water from dredged material containment areas is one potential problem that has become apparent. This study investigated the potential contamination of receiving waters by oil and grease in return waters from dredged material containment areas.

This study was originally planned to involve three work areas, these being:

a. An appraisal of the magnitude of the problem of oil and grease discharges from dredged material containment areas.

b. The development of a means to predict the appearance of significant levels of oil and grease in return waters.

c. The evaluation and development of candidate treatment processes for reduction of the oil and grease content of return waters.

Field studies were undertaken at six locations where dredging is practiced. The six sampling sites were located in three geographical regions including the Texas Gulf Coast, the Great Lakes, and the Atlantic Coast. Sediment samples and water samples, from both the water column at dredging sites and return water from containment areas, were gathered and subsequently analyzed.

Among the sediment characteristics measured in the field studies were oil and grease concentration, solids content, fraction of nonpolar oil, porosity, particle-size distribution, and elutriate oil and grease concentration. Water column measurements included oil and grease concentration, total suspended solids concentration, total residue concentration, dissolved oxygen concentration, conductivity, and pH. The oil and grease content (both total and nonpolar oil) and total suspended solids concentration of containment area return waters were monitored.

Concurrent with the field studies, a review of potential oil and grease treatment methods was conducted. Two potential treatment methods, termed "end-of-pipe management" and "source management," were reviewed

and their potential applicability to dredging was investigated. End-of-pipe management involves on-site treatment of the return water to reduce the oil and grease level prior to discharge. Source management would involve either: (1) increasing the sorptive capacity of dredged materials for oil and grease by the addition of sorptive material such as activated carbon to the slurry prior to discharge to the containment area or (2) arrangement and manipulation of the sediments within the containment area to maximize retention of oil and grease. End-of-pipe treatment methods using conventional wastewater treatment processes appeared more favorable than potential source management techniques for reducing the oil and grease content of return waters.

The results of the field study strongly indicated that oil and grease do not appear to be released to a significant extent from sediments during the dredging process. The oil and grease content of containment area return waters was generally less than 5 mg/l. The highest concentrations of oil and grease in return waters were detected at times when elevated suspended solids levels were also found.

A modified form of the standard elutriate test was used in assessment of the potential release of oil and grease from sediments. The elutriate test is designed to measure the amount of any pollutant that migrates from the sediment to the water as a result of dredging. Oil and grease levels in the elutriate were quite low, even with extremely oily sediments, and were sometimes actually less than concentrations measured in the diluent water used in the test, indicating that oil and grease was sorbed from the solution onto the sediments.

Attempts to correlate the release of oil and grease from sediments during dredging operations with various environmental parameters were unsuccessful. Consistent relationships were not found among the field study data, although oil and grease did appear to be more tightly bound to sediments in saline water than in fresh water. Likewise, efforts to relate physical sediment characteristics to oil and grease content proved fruitless.

Using data gathered during the field survey as well as from bench-scale studies (discussed in subsequent paragraphs), an evaluation of oil

and grease sampling and analytical techniques was performed. It was determined that there is a high level of analytical variability in oil and grease measurements, particularly in the low concentration range evaluated in this study.

At this point (the conclusion of the first phase of the study), plans for the remainder of the study were reassessed. It was decided to redirect the efforts of the study to determination of significant environmental factors affecting the release of oil and grease from dredged sediments. Confirmation of the field study results, which indicated that oil and grease were not released from sediments by dredging operations, was another new objective of the revised study. Providing that the results of the second phase of the study were consistent with previous findings, no further evaluation of treatment methods would be conducted.

A series of bench-scale experiments was devised to evaluate the relationship of oil and grease release to several variables, among them salinity, pH, temperature, and the degree and duration of mixing. The range of conditions evaluated for each of these variables encompassed essentially all conditions likely to occur in the field during actual dredging operations. The results of the bench-scale studies showed no consistent relationship between the various environmental factors and oil and grease release from dredged sediments. The quantity of oil and grease released, even under the most severe conditions established by these studies, was not appreciably different from levels measured during the field surveys.

The overall conclusion of this study is that oil and grease are not released from sediments in significant quantities as a result of dredging. When high oil concentrations are observed in return waters, these are associated with high suspended solids concentrations and the oil is sorbed on the solids. Any treatment above and beyond temporary containment to remove suspended particles is not warranted based on the results of this study.

PREFACE

The work described in this report was sponsored by the U. S. Army Engineer Waterways Experiment Station (WES, Vicksburg, Mississippi) Dredged Material Research Program under Task 6B (Treatment of Contaminated Dredged Material), Work Unit 6B05 (An Evaluation of Oil and Grease Contamination Associated with Dredged Material) of the Disposal Operations Project (DOP). The research was performed by Engineering-Science, Inc. (ESI) in Austin, Texas, and Berkeley, California. The report presents the results of laboratory and field investigations performed to evaluate oil and grease contamination associated with dredged material. The investigation was conducted under the supervision of Dr. L. F. Tischler, Manager, ESI Austin Office. Dr. J. N. Chieu assisted in the planning of the project, directed the field sampling efforts, and wrote portions of the report. Mr. T. A. Helbig, Manager of the ESI Laboratory in Berkeley, California, was responsible for all analytical work and the conduct of the bench-scale studies. Mr. R. L. Elton, Ms. V. L. Slonek, and Mr. C. T. White were responsible for data evaluation and analysis and various aspects of report preparation. Mr. White prepared the final report.

ESI would like to acknowledge the assistance of the U. S. Army Corps of Engineer staff in four Districts: Buffalo, Galveston, Detroit, and Savannah. The support of the District personnel was essential to the conduct of the field surveys described in this report. The Districts provided data from previous surveys and assisted in the sampling logistics, and the Galveston District collected samples at certain locations to supplement samples collected by ESI.

The research was monitored by Dr. J. L. Mahloch of the Environmental Effects Laboratory, WES, and Mr. T. K. Moore, Task 6B Manager. ESI project staff acknowledges the valuable technical review provided by Dr. Mahloch and Mr. Moore. Mr. C. C. Calhoun, Jr., Manager, DOP, was the designated Contracting Officer's representative for this contract. Commanders and Directors of WES during the conduct of the study and publication of the report were COL G. H. Hilt, CE, and COL J. L. Cannon, CE. Technical Director was Mr. F.R. Brown.

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CONVERSION FACTORS, METRIC (SI) TO U. S. CUSTOMARY AND U. S. CUSTOMARY TO METRIC UNITS OF MEASUREMENT

Metric (SI) units of measurement used in this report can be converted to U. S. customary units as follows:

Multiply	By	To Obtain
Metric (SI) to U. S. Customary		
metres	3.281	feet
square metres	10.76	square feet
millilitres	2.642×10^{-4}	gallons
litres	0.2642	gallons
milligrams	2.205×10^{-6}	pounds (mass)
grams	0.0022	pounds (mass)
kilograms	2.205	pounds (mass)
cubic metres per second	22.83	million gallons per day
cubic metres per square metre per second	1,473.0	gallons per minute per square foot
Celsius degrees	1.8	*Fahrenheit degrees**
U. S. Customary to Metric (SI)		
microns	3.937×10^{-5}	inches
miles (U. S. statute)	1.609344	kilometres
gallons (U. S. liquid)	0.003785412	cubic metres
tons (short)	907.1847	kilograms

* To obtain Fahrenheit degrees from Celsius readings, use the following formula: $F = 1.8(C) + 32$.

AN EVALUATION OF OIL AND GREASE CONTAMINATION ASSOCIATED WITH DREDGED MATERIAL CONTAINMENT AREAS

PART I: INTRODUCTION

Background

1. The environmental consequences of dredging for maintenance of navigable channels have become a major concern to the Corps of Engineers and regulatory agencies. This environmental concern initiated several intensive research studies related to dredged material disposal under the direction of the Dredged Material Research Program (DMRP). One of the research interests in the DMRP is the potential oil and grease contamination associated with the dredging of sediments and the return water from dredged material containment areas.

2. It is important to note that a wide range of substances are detected in the measurement of oil and grease in waters and sediments. Rather than a specific substance, oil and grease includes several types of compounds; among these are hydrocarbons, fatty acids, soaps, fats, waxes, and oils. The substances detected in the measurement of oil and grease share common physical properties, chiefly their solubility in the particular solvent (usually freon) employed in the laboratory analysis. Because of the diversity of compounds measured by the test and because of the variable solubility of these compounds in different solvents, oil and grease are actually defined by the particular laboratory technique utilized for their determination.

3. Oil and grease has been a significant environmental problem in many instances. Major oil pollution sources include normal industrial operation, accidental spills, and intermittent discharges from ships and tankers. The primary oil loss in 1969 alone was approximately 20 million tons. These pollution sources may be further subcategorized as follows:[1]

Tanker	25.4 percent
Other ships (bilge water, etc.)	24.0 percent
Accidental spills	9.6 percent
Refinery petrochemical wastes	14.4 percent
Off-shore production	4.8 percent
Rivers carrying industrial wastes	21.6 percent

A portion of this lost oil ultimately ends up in sediments. Periodic maintenance dredging of navigable waters may result in resuspension of oil and grease adsorbed or trapped in the sediment. Because of dredging, oil may be released to the receiving water or suspended in the return waters from containment areas.

4. Return water from dredged material containment areas is not regulated as a point-source discharge.[2] The effluent quality is monitored outside the mixing zone, rather than at the discharge point. If the level of oil and grease outside the mixing zone complies with the specified water-quality standards for the receiving water body, no treatment is required for the return water. This regulation provides additional flexibility for the mixing of the return water with the receiving water body. Should the oil and grease level outside the mixing zone exceed the quality standard, the discharge from the diked area must be treated to a level such that the oil and grease concentration outside the discharge mixing zone will comply with the appropriate limit.

5. In the past, water-quality criteria for oil and grease were usually couched in general terms, such as prohibitions on the appearance of visible surface accumulations of oil or requirements that oily substances do not interfere with the beneficial uses of the receiving waters. The most recent U.S. Environmental Protection Agency (EPA) publication on water-quality criteria has established permissible levels of oil and grease in water in more explicit terms:

a. "0.01 of the lowest continuous flow 96-hour LC50 to several important freshwater and marine species, each having a demonstrated high susceptibility to oils and petrochemicals.

b. Levels of oil or petrochemicals in the sediment which cause deleterious effects to the biota should not be allowed.

c. Surface waters shall be virtually free from floating non-petroleum oils of vegetable or animal origin, as well as petroleum derived oils."[3]

The diversity of compounds included in the category of oil and grease is recognized in the EPA report and 96-hour LC50 levels for specific compounds and petroleum products are therefore presented. Since sediments can contain a wide variety of compounds classified as oil and grease, the significance (in terms of the latest EPA criteria) of oil and grease concentrations in containment area return flows can only be established by identification of the particular types and concentrations of these oily constituents.

6. One frame of reference for evaluating the significance of oil and grease concentrations in containment area return flows is the point-source discharge limitations for oily wastewaters that have been established by the U.S. Environmental Protection Agency (EPA) and other regulatory agencies. Although containment area return flow has not been defined as a point source, the various point-source limitations serve as a basis for defining technologically feasible levels of effluent oil and grease. A discharge requirement limiting the oil and grease content of storm water runoff from tank fields and nonprocess areas of petroleum refineries was promulgated by EPA.[4] This requirement set a maximum permissible concentration of 15 mg/l of oil and grease in "clean" storm water discharges. Though this effluent limitation has been remanded in a recent court decision, the 15-mg/l limit is informative in that it apparently represents a level of treatment considered to protect water quality.

7. Effluent-quality criteria for point-source discharges to certain receiving waters are summarized in Table 1. One can infer from these limitations that there is generally a maximum acceptable limit of from 10 to 20 mg/l of oil and grease in wastewaters.

Table 1

Effluent-Quality Criteria
for Point-Source Discharges to Surface Waters*

Description of Surface Waters	Oil Concentration** mg/l
Hampton Road Port	
James River	10
York River	10
Atlantic Ocean	10
New York Port	
New York Harbor	1.0
Galveston/Houston Port	
Galveston Bay	20
Houston Ship Channel	20
Cleveland Port	
Lake Erie	10
St. Louis Port	
Mississippi River	15
Miami/San Juan Port	
Biscayne Bay	10
Bahia de San Juan	10
San Diego Port	
Pacific Ocean	10
San Francisco Port	
San Francisco Bay	15

* Reference 5

** Hexane-soluble oil.

Purpose and Scope of Study

8. The purpose of this study is to evaluate the potential problem of oil and grease contamination associated with dredged material containment areas. The original scope of this study may be described in terms of three primary objectives:

a. To assess the magnitude of oil and grease contamination of waters associated with dredged material containment areas.

b. To develop a method for predicting whether significant quantities of oil and grease will be present in containment area return waters.

c. To evaluate different treatment processes that could feasibly be utilized for the removal of oil and grease from return waters.

9. It was planned to accomplish the original objectives of the study in the format of a two-phase work program. Objectives "a" and "b" would be accomplished in the first phase of the study along with a portion of objective "c," that being a review of the literature on potential treatment methods. The second phase of the study would then concentrate on the viable treatment options, eventually leading to the development of treatment methods for possible full-scale implementation in the field.

10. As a result of the findings of the first phase of the study, the scope of the second phase was changed. Rather than investigate potential treatment methods, additional studies were performed on the mechanisms of oil release from sediments. Bench-scale studies were devised to confirm or refute the findings of the field study and to investigate the significant environmental factors that may affect the release of oil from sediment during dredging operations. An additional purpose of the bench-scale studies was to establish whether or not treatment is required to reduce the oil and grease content of containment area return waters. If it were established that oil and grease is a problem in discharges from dredged material containment areas, treatment methods for the reduction of oil and grease levels in return waters would be further evaluated.

PART II: OIL AND GREASE SAMPLING AND ANALYTICAL TECHNIQUES

11. This part addresses the analytical capabilities and statistical reliability of tests used for the measurement of oil and grease in waters and sediments. A discussion of the factors affecting the collection of representative samples is presented. Alternative methods of extraction and detection of oil and grease are discussed, and a statistical analysis of the analytical characteristics of these methods is presented.

Sampling Techniques

12. It is extremely difficult to obtain a representative sample in a multiphase system, such as oil-water mixtures in both sediments and natural water bodies. The sampling technique can bias the estimated oil and grease content in either direction. In order to minimize this sampling bias, special containers and procedures are required for oil and grease sampling.[6] For example, plastic bottles or caps lined with polyethylene or waxed paper cannot be used as they are a source of extractable constituents. Handling of the bottles is also critical as there is enough body oil on hands or fingertips to severely contaminate a sample at low concentration levels.

13. The location and nature of the sampling station is critical in obtaining representative oil and grease samples. Fast moving waters exhibiting turbulent flow are preferable for collection of water samples, but, unfortunately, it is often necessary to take samples from waters having low levels of turbulence and mixing. A varying oil and grease concentration profile with depth is often characteristic of nonturbulent flow, and a sample bias is introduced if the water is withdrawn from the bottom, where organic compounds may be collected; the surface, where free oil may have accumulated; or the middle section, which may be essentially free of compounds detected by the oil and grease test. The degree of sampling bias alone is particularly significant when

considering dilute concentrations of total oil and grease in the range from 1.0 to 20 mg/l.

14. In regard to sampling sediments for oil and grease, the major consideration is the possibility that there may be "pockets" of high or low concentrations, depending upon the hydraulic characteristics of the water body and other factors. This problem, however, is not peculiar to oil and grease and is the same for the measurement of any chemical parameter. Nevertheless, if a sufficiently large sediment sample is taken and then homogenized thoroughly before analysis, it is likely that the relative margin for error in the oil and grease measurement is less than that for water samples, particularly due to the typically large quantity of oil and grease present in sediments as compared to the water phase.

Analytical Techniques

15. The analytical techniques associated with the measurement of oil and grease that are evaluated in this section are: (1) gravimetric and infrared detection, (2) freon and hexane extraction, (3) the drying of sediment samples by both the oven-drying method and the magnesium sulfate method, and (4) the sheen test and its relationship to other analytical methods.

16. The freon extraction-gravimetric detection method for oil and grease determination in wastewaters has been specified by the EPA as an approved method.[7] The freon extraction-infrared detection method had been proposed as an equivalent technique in the original EPA regulation, but it was dropped in the final version. A recent "oil and grease precision round robin" study of these methods was conducted by the American Society of Testing and Materials (ASTM). American Petroleum Institute (API) members, the EPA, and private commercial laboratories participated in this study. Replicate samples containing oil and grease at six concentration levels were sent to 31 laboratories for analysis. Results for the freon extraction-gravimetric detection and freon extraction-infrared detection methods were reported by 22 and 17 of these laboratories, respectively.

17. The results for the freon extraction-gravimetric procedure were statistically analyzed for this study. The Student's t-test was used to eliminate results that were possibly erroneous, and only those data within the 90-percent confidence interval were used to estimate the "true value" of oil and grease content for each of the six samples sent to each laboratory. Variation between sample concentrations and between values obtained from the different laboratories was compared using a two-way analysis of variance. An absolute error parameter, equal to the absolute value of the log of the individual analytical value divided by the "true value" of the sample, was calculated and plotted against the "true value" of the sample as shown in Figure 1. These analyses indicated that the oil concentration affected the absolute error, but the use of one laboratory or another did not.

18. A least squares regression of the absolute error as a function of oil and grease concentration is shown in Figure 1. The effect of "true" concentration on the degree of analytical variation can be calculated directly from this graph. These calculations are tabulated in Table 2 for the freon extraction-gravimetric detection method.

19. The concentration range shown in Table 2 represents the range of oil and grease concentrations that could be expected to be measured by 95 percent of the participating laboratories if the "true" sample concentration is as stated in the table. It is emphasized that these data represent variations between laboratories and do not represent the precision of the analysis within a laboratory. The latter information is impossible to obtain from the round-robin data base although it is an important consideration in assessing the usefulness of the analytical technique and will be discussed in a subsequent section.

20. The infrared detection method shows similar analytical variability. A comparison of the round-robin results using infrared and gravimetric detection methods is shown in Table 3. The results of the "precision round robin" demonstrate that the two detection methods for oil and grease do not give equivalent results. The infrared method shows a uniformly higher oil and grease concentration on the same sample as compared to gravimetric detection. This phenomenon is termed "yield."

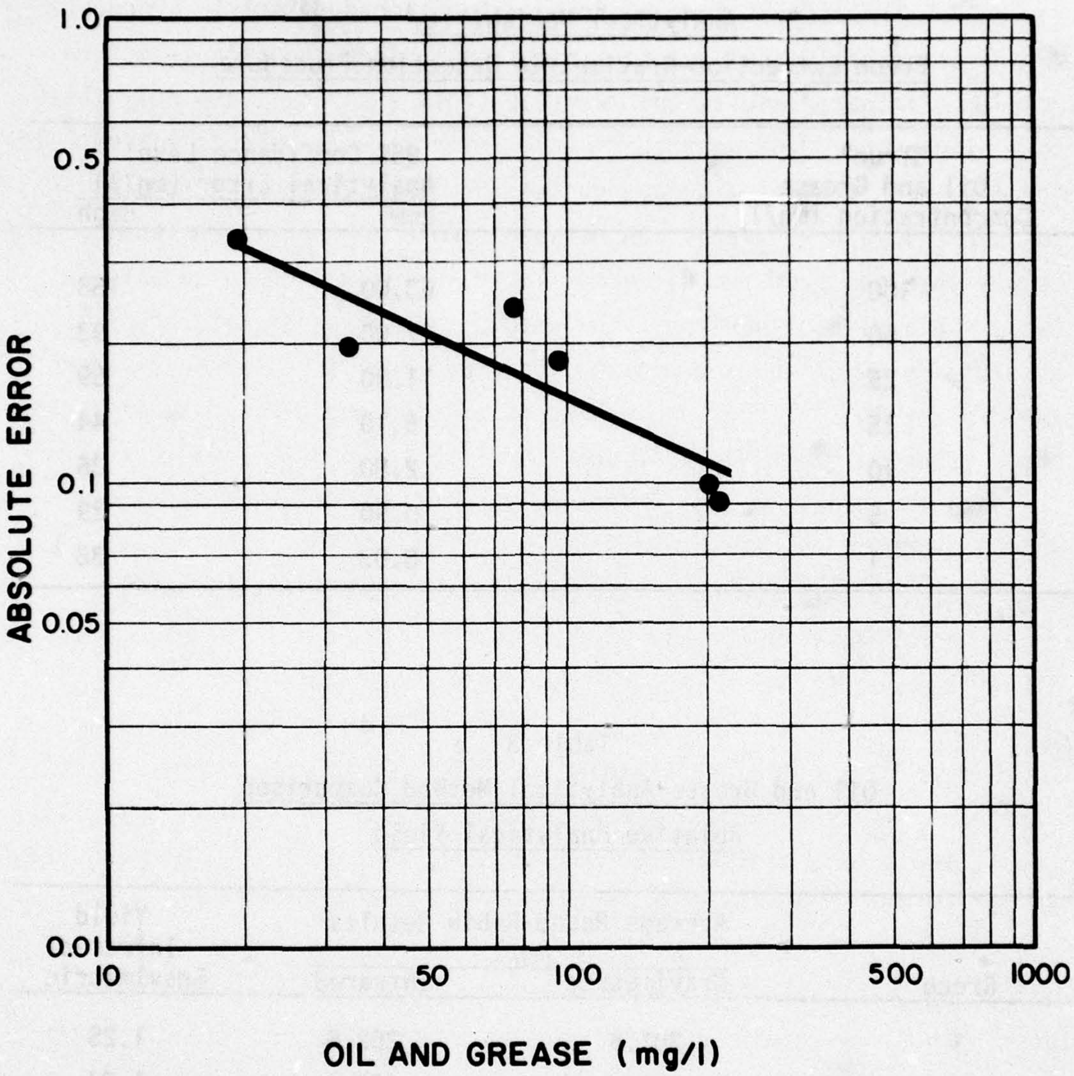

Figure 1. Absolute Error of Oil and Grease Determination by Freon Extraction-Gravimetric Procedure as a Function of Concentration

Table 2

Analytical Variability

Freon Extraction-Gravimetric Detection Procedure

"True" Oil and Grease Concentration (mg/l)	95% Confidence Level Analytical Error (mg/l) Low	High
100	63.00	158
50	27.00	93
25	11.00	59
15	5.10	44
10	2.80	36
5	0.90	29
1	0.03	38

Table 3

Oil and Grease Analytical Method Comparison

Relative Analytical Yield

Group	Average Round-Robin Results* mg/l Gravimetric	Infrared	Yield Infrared/ Gravimetric
1	201.5	252.6	1.25
2	206.5	262.6	1.27
3	90.4	130.5	1.44
4	75.1	111.8	1.49
5	31.7	48.2	1.52
6	17.4	23.4	1.34

* All data within ±2 standard deviations of "true value."

As Table 3 indicates, the infrared detection method yields at least 25 percent more than the gravimetric method. In the lower concentration ranges (group 5), the yield can be as much as 52 percent greater for the infrared method. Since almost all oil and grease data for effluents and natural water bodies that were collected in the past were based on variations of the gravimetric detection method, and since most regulations for this parameter are based on these data, serious error can be introduced in evaluations of comparative water quality if the infrared detection method is used.

21. Another result of the "precision round robin" was to show the high potential for extreme errors in the estimates of oil and grease concentration in single samples and by certain laboratories. The statistical analyses shown in Figure 1 and Table 2 were done using only data passing a 90-percent confidence level t-test. Data from two participating laboratories were not used in this analysis: one had uniformly very high concentrations for all samples, and the other was always very low. These characteristics were very obvious with only a visual review of the data base. The initial data base contained 131 gravimetric determinations of oil and grease. After applying the stated rejection criterion, 107 data points were used to estimate the "true values." The relatively large amount of data discarded reveals the high potential for error in this analysis.

22. A similar statistical analysis was conducted using the freon extraction-infrared detection method data collected during the round robin. The results of this analysis are shown in Table 4. These data show that the infrared detection method has lower analytical variability than the gravimetric method, particularly at low concentrations. However, a major problem with the infrared method is the selection of the "standard" oil and grease that is used to provide the measurement basis. The infrared method utilizes a known oil and grease standard to determine the spectral bands for comparison with the field samples. If the composition of the standard and the sample are similar in terms of the properties of the hydrocarbons (aliphatics, aromatics, etc.), then the test is quite accurate. However, its utility for samples of unknown composition, such as sediment samples, is considerably more suspect.

Table 4

Analytical Variability

Freon Extraction-Infrared Detection Procedure

"True" Oil and Grease Concentration (mg/l)	95% Confidence Level Analytical Error (mg/l) Low	High
100	78.00	129.0
50	38.00	67.0
25	18.00	35.0
15	11.00	21.0
10	7.00	15.0
5	3.20	7.7
0	0.56	1.8

Statistical Evaluation of Data Collected in Bench-scale and Field Studies

23. Bench-scale studies were conducted to determine the effect of various environmental factors on the release of oil and grease from sediments during the dredging process. These studies are described in Part V. In the bench-scale studies, oil and grease analyses were run in triplicate on samples subjected to various physical and chemical conditions. Along with the results of the field studies, the results of the bench-scale studies can be used in assessing the precision of oil and grease measurements made using the freon extraction-gravimetric detection technique.

24. It is important to note that for each of the three analyses performed in the bench-scale studies under a particular set of environmental conditions, a separate and distinct sediment sample was extracted from the bulk of the homogenized sample and a separate test procedure was run. In this manner, the variation in the results of the bench-scale analyses reflects the variation of the overall procedure utilized rather than of any one portion (i.e., the freon extraction-gravimetric detection technique). It is, in fact, suprising that the results show so little variation when one considers the factors that could possibly account for variability (e.g., variation between samples in both consistency and oil and grease content; variation in the conduct of the test procedure; variation in the processing of samples; and variation in the extraction and detection of oil and grease).

25. Since the supernatant oil and grease concentrations detected for the various environmental conditions varied somewhat (i.e., the triplicate analyses had average oil and grease concentrations ranging from 1 to 12 mg/l), it was first necessary to obtain a uniform basis upon which the results can be compared. This has been accomplished by determination of the ratio of the oil and grease concentration detected in an individual analysis to the average concentration of the triplicate analyses conducted under identical environmental conditions. By definition, these ratios will have a mean value of unity. With all of the

data on a common basis, the distribution of the calculated ratios can be examined and an estimate of the variability of the test procedure prepared. As is shown in Figure 2, the calculated ratios follow a normal distribution with a mean value of approximately unity. Curves for both total and nonpolar oil and grease are presented, with standard deviations of 0.33 mg/l and 0.31 mg/l, respectively. These values reveal that about two-thirds of all individual oil and grease measurements are within a range of 67 to 133 percent of the mean value of the triplicate analyses.

26. Data from the bench-scale studies can be compared on two other bases. Figure 3 is a linear regression plot of the mean oil concentration of the triplicate analyses versus the standard deviation of the same analyses. Correlation coefficients of 0.62 and 0.56 were determined for total and nonpolar oil and grease, respectively. Figure 4, which is more informative than the preceding figure, is a plot of the coefficient of variation (equal to the quotient of the standard deviation divided by the mean) versus the mean oil concentration. It had been expected that these two parameters would show an inverse relationship: that is, for low oil and grease concentrations, the coefficient of variation would be high, and, conversely, for high oil and grease concentrations, the coefficient of variation would be low. The data, however, do not bear out this relationship, indicating that, in the range of oil and grease concentrations detected (i.e., 0 to 15 mg/l), the repeatability of the procedure is essentially independent of the oil and grease concentration. For higher concentrations, the data appear to show a trend in the reduction of the coefficient of variation; however, this reduction is insignificant in the range of concentrations analyzed.

27. Data taken during the field sampling phase of this study can be evaluated with regard to the accuracy and precision of the freon extraction-gravimetric detection technique. Triplicate analyses for oil and grease were conducted on sediment samples prepared in accordance with the modified standard elutriate procedure (this procedure is described in Appendix A). The variation in the field study data can be directly attributed to the inherent variability of the extraction and

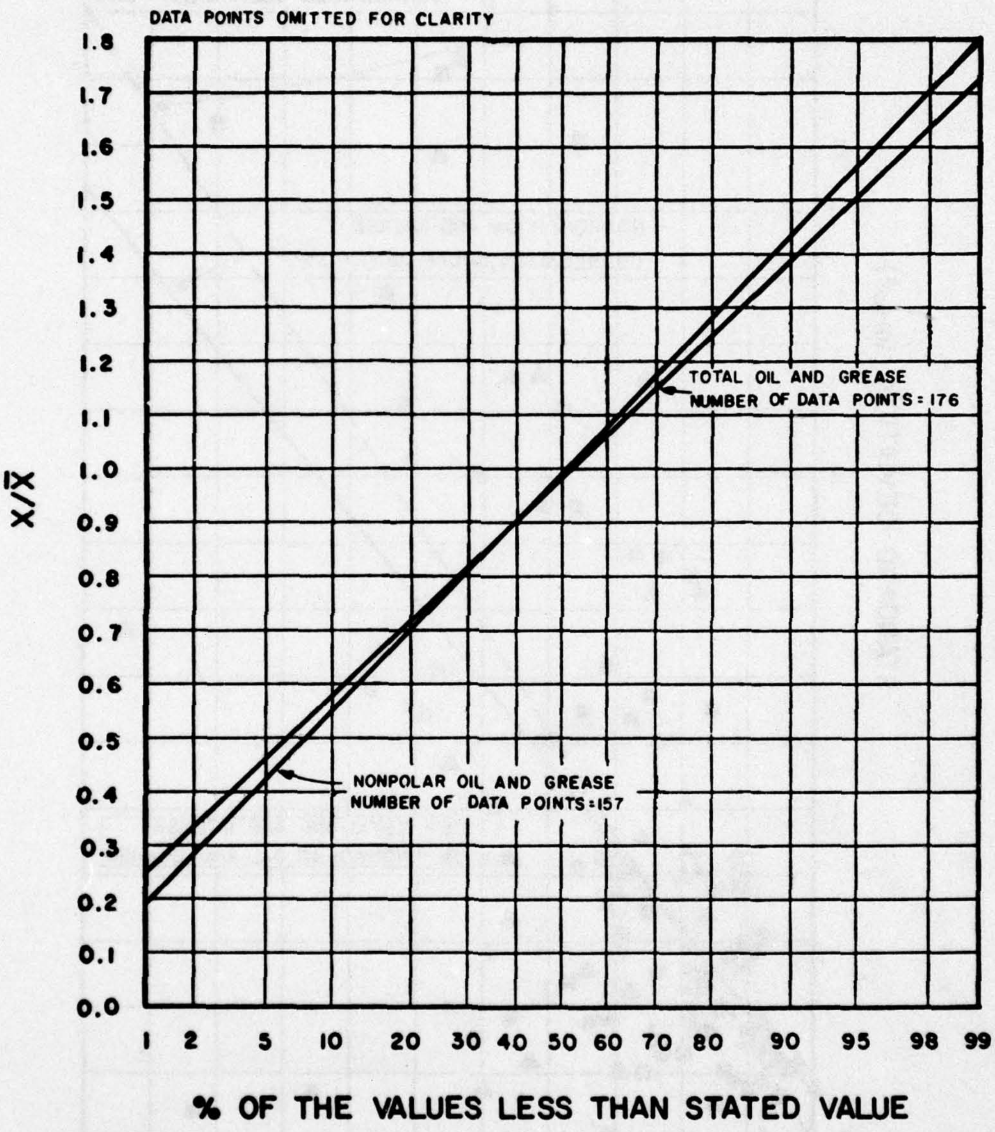

Figure 2. Probability Distribution of Normalized Values $X/\overline{X}$ - Bench-scale Study Data

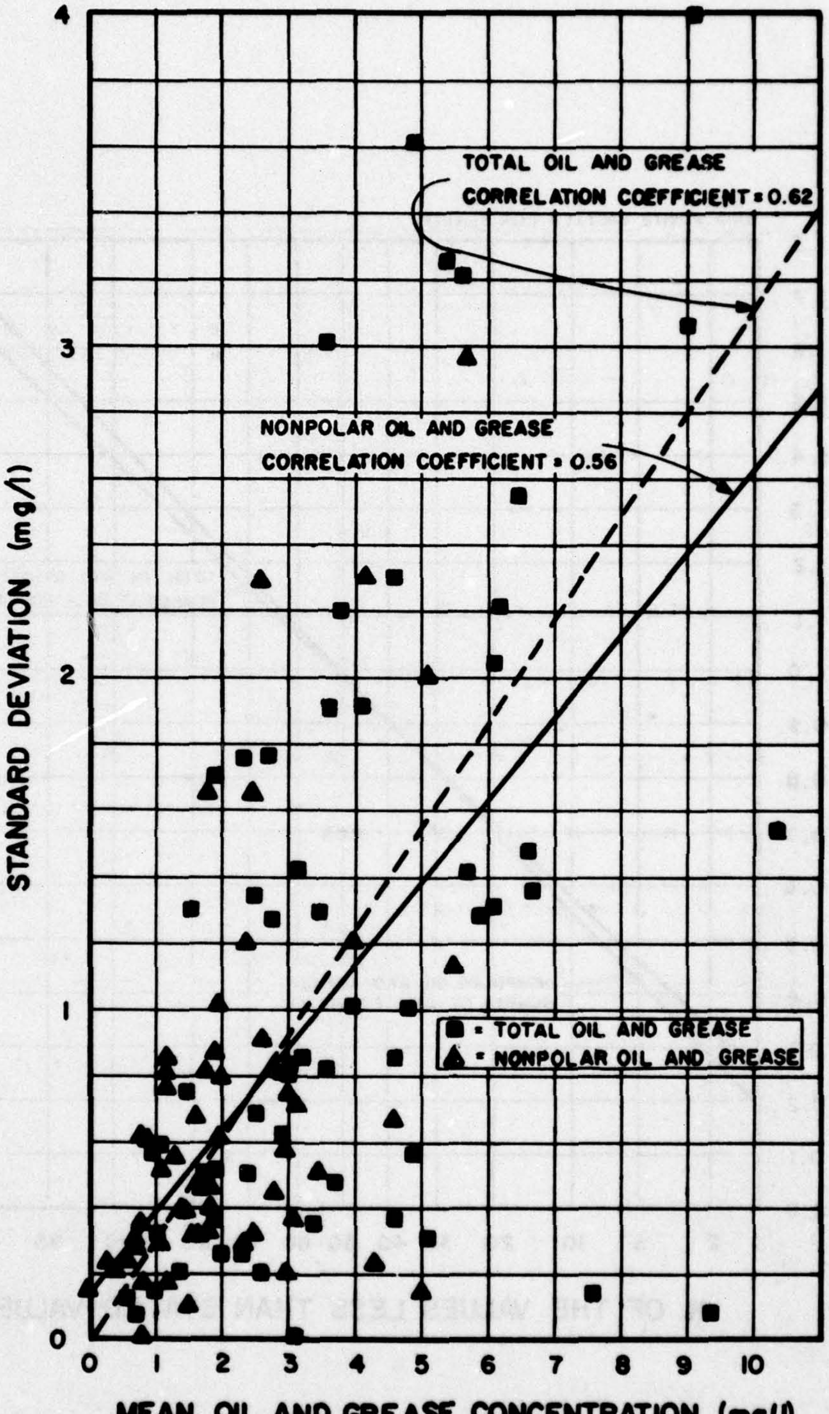

Figure 3. Mean Oil and Grease Concentration of Replicate Analyses versus Standard Deviation of Oil and Grease Concentrations - Bench-scale Study Data

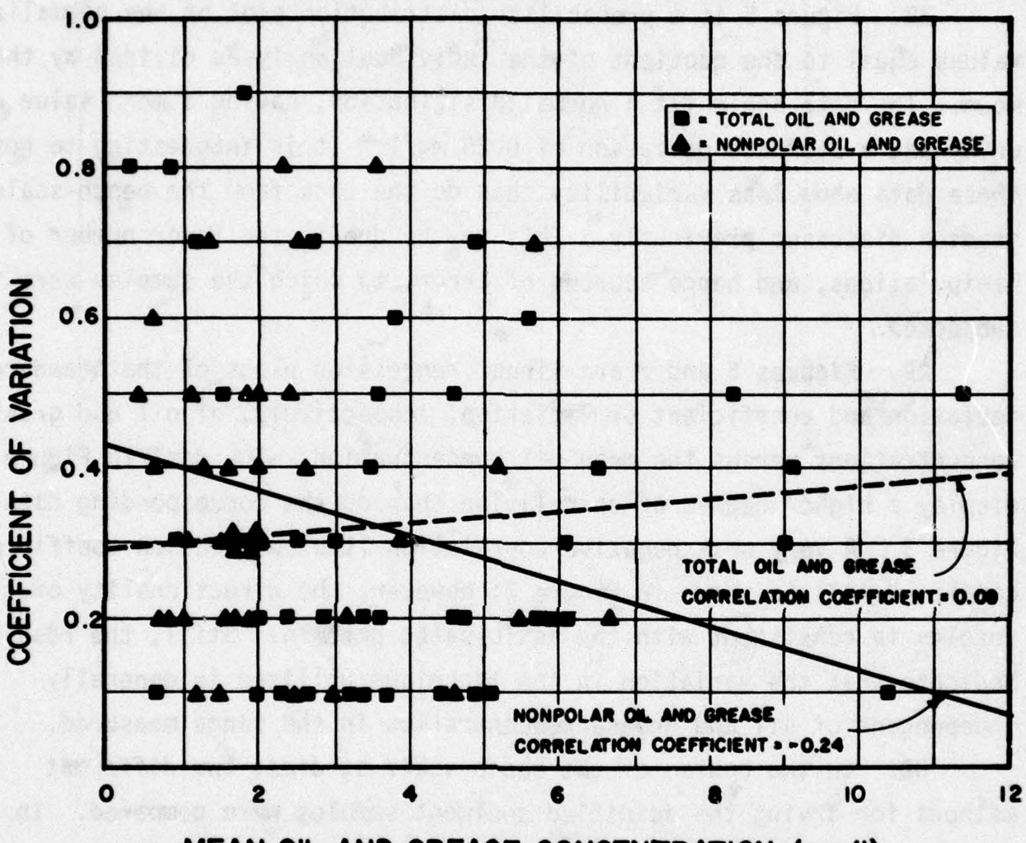

Figure 4. Mean Oil and Grease Concentration of Replicate Analyses versus Coefficient of Variation of Oil and Grease Concentrations - Bench-scale Study Data

detection technique that was employed. Three figures, corresponding to the graphical displays for data accumulated during the bench-scale studies, are presented.

28. Figure 5 is a probability distribution plot of the normalized values equal to the quotient of the individual analyses divided by the mean. The data again fit a normal distribution, having a mean value of unity and a standard deviation of 0.25 mg/l. It is interesting to note these data show less variability than do the data from the bench-scale studies discussed previously. This may be due to the fewer number of manipulations, and hence sources of error, to which the samples were subjected.

29. Figures 6 and 7 are linear regression plots of the standard deviation and coefficient of variation, respectively, of oil and grease concentrations versus the mean oil concentration. The data in Figure 6 display a higher degree of correlation than do the corresponding data in Figure 3. A very weak negative correlation (the correlation coefficient equals -0.143) is shown in Figure 7; however, the directionality of the results is consistent with the anticipated pattern. Still, the results indicate that the variation in the technique utilized is generally independent of oil and grease concentration in the range measured.

30. In the course of the bench-scale studies, two different methods for drying the acidified sediment samples were compared. In the oven-drying method, the acidified sample is oven-dried at 103°C for a period of 24 hours in a manner similar to the total suspended solids test (see Appendix A). The alternative method (see Appendix A), which reportedly yields higher results, uses magnesium sulfate monohydrate to dry the sample. Both methods have drawbacks. Oven-drying may lead to the oxidation of a portion of the oil and grease in the sample. When magnesium sulfate is used for drying, crystals of magnesium sulfate (as verified by atomic adsorption) appear as the solvent is evaporated. If extreme care is taken to add only the minimum amount of magnesium sulfate necessary for drying, the appearance of crystals is kept to a negligible amount. With extremely oily samples, however, it is difficult to observe the dryness of the sample, thereby making the addition of

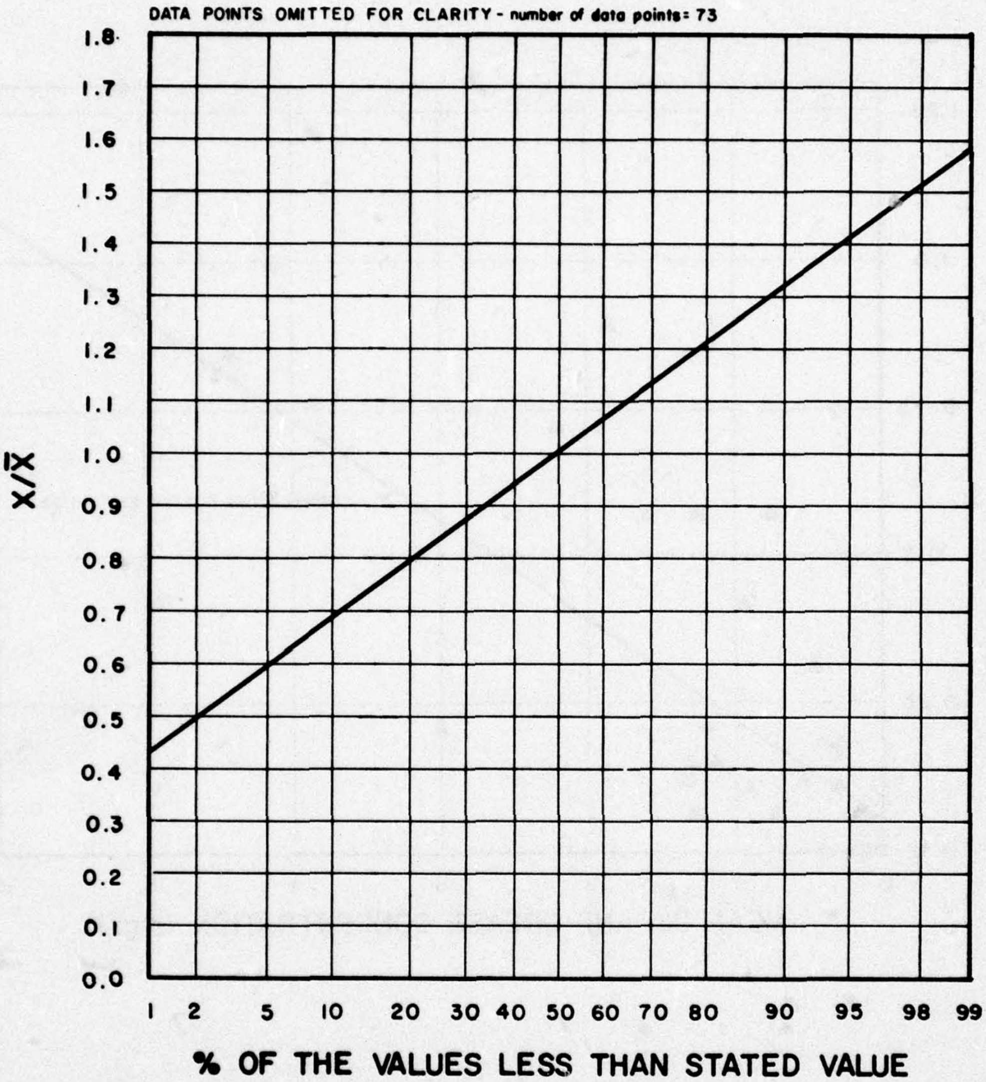

Figure 5. Probability Distribution for Normalized Values of X/$\overline{X}$ - Field Study Data

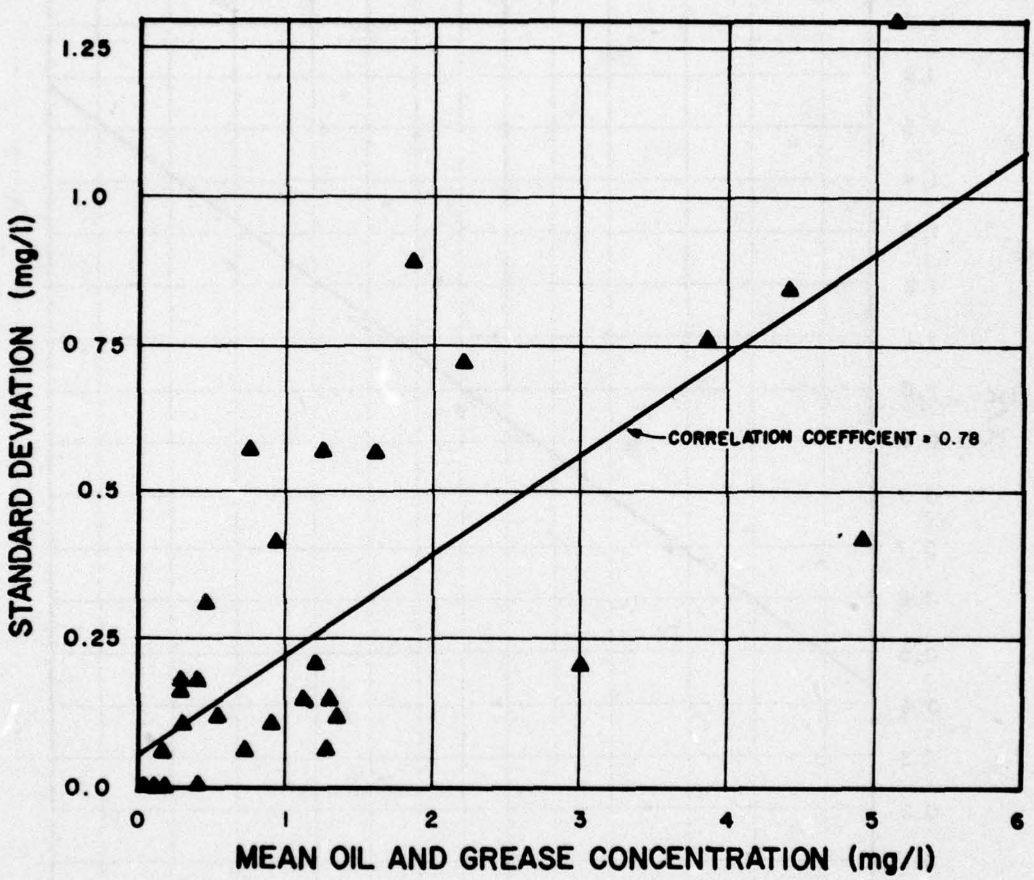

Figure 6. Mean Oil and Grease Concentration of Replicate Analyses versus Standard Deviation of Oil and Grease Concentrations - Field Study Data

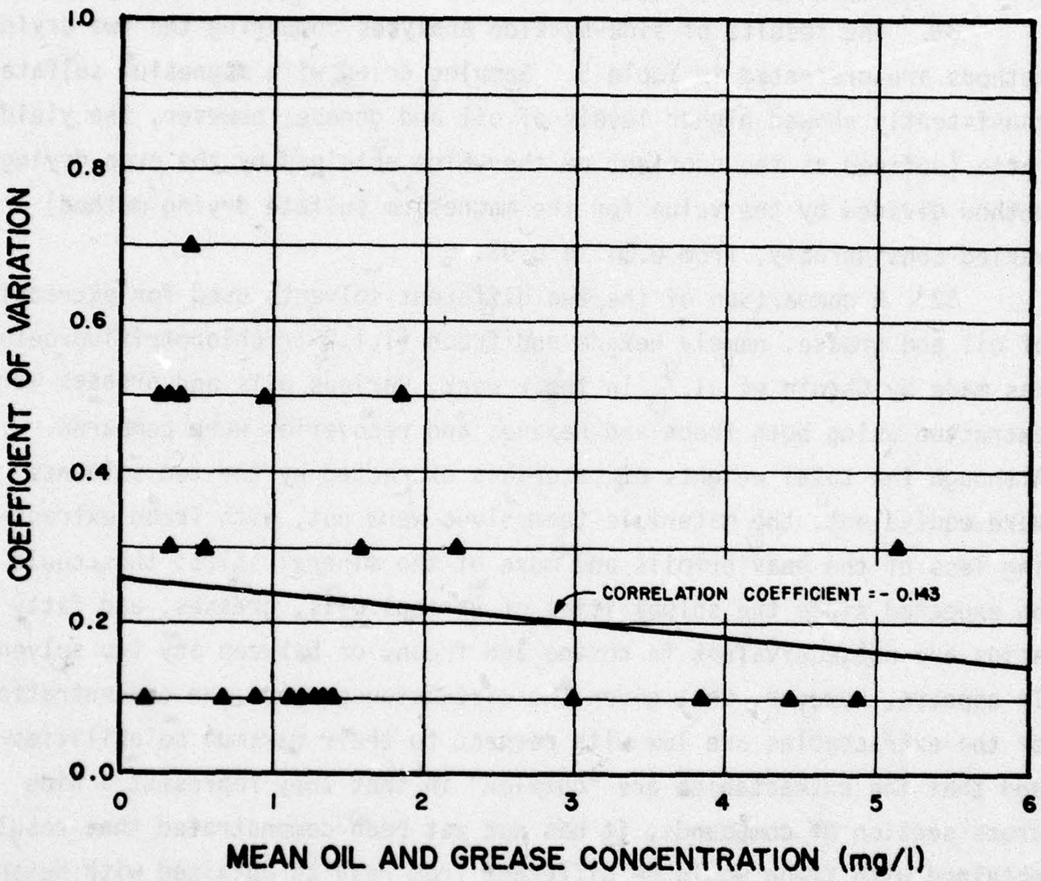

Figure 7. Mean Oil and Grease Concentration of Replicate Analyses versus Coefficient of Variation of Oil and Grease Concentrations - Field Study Data

magnesium sulfate a difficult task. Different results between techniques cannot be attributed to evaporation, as equivalent temperatures are attained during the evaporation of the solvent in the weighing step. Losses may also occur upon transfer and grinding of the dried sample for soxhlet extraction.

31. The results of side-by-side analyses comparing the two drying methods are presented in Table 5. Samples dried with magnesium sulfate consistently showed higher levels of oil and grease; however, the yield ratio (defined as the quotient of the value obtained by the oven-drying method divided by the value for the magnesium sulfate drying method) varied considerably, from 0.14 to 0.93.

32. A comparison of the two different solvents used for extraction of oil and grease, namely hexane and freon (1,1,2-trichlorotrifluoroethane), was made by Chanin et al.[8] In their work, various oils and greases were extracted using both freon and hexane, and recoveries were compared. Although the total weights of materials extracted by the two solvents were equivalent, the materials themselves were not, with freon extracting less of the heavier oils and more of the mineral salts; this could be expected since the solubilities of various oils, greases, and fatty acids are not equivalent in hexane and freon, or between any two solvents. It appears, however, that given the circumstances that the concentrations of the extractables are low with respect to their maximum solubilities and that the extractables are "complex" in that they represent a wide cross section of compounds, it has not yet been demonstrated that results obtained with freon would be different from results obtained with hexane.

33. In addition to being nonflammable, freon is denser than water, which makes it particularly convenient for use in separatory funnel extractions. Losses arising through transferring the sample are likely to be smaller using freon as the solvent.

34. Another test, namely the sheen test, has been mentioned as a possible indicator of contamination by oil and grease. This test has recently been incorporated in the EPA regulations for ocean dumping.[9] The regulation states that the total amount of oil and grease in the waste materials shall "not produce a visible surface sheen in an undisturbed water sample when added at a ratio of one part waste material to

Table 5

Results of Sediment Oil and Grease Analyses Using Two Drying Methods

	Drying Method Used				
	Oven-Dried		$MgSO_4$		Yield
Sample Number	Mean Oil Level mg/kg	Standard Deviation	Mean Oil Level mg/kg	Standard Deviation	Oven-Dried/$MgSO_4$ (mg/kg)/(mg/kg)
PA-1	19,570	2,790	33,120	10,905	0.59
PA-2	223	46	1,543	337	0.14
HSC-3	1,539	328	1,648	155	0.93
HSC-8	278	92	680	164	0.41

Note: HSC - Houston Ship Channel, Texas
PA - Sabine Neches Canal in Port Arthur, Texas

100 parts of water." Because the sheen test is based on visual inspection, the test is subjective and is not usually used as an analytical technique for the measurement of oil and grease.[10] The test is too imprecise to have any practical use in the measurement of oil and grease and there is no apparent method of relating sheen to oil and grease concentrations estimated using the analytical techniques previously described.

Summary

35. Representative sampling of multiphase systems is difficult, and the degree of bias that can be introduced diminishes the reliability of results of the oil and grease analysis, particularly at low concentrations.

36. The round-robin program discussed in this part demonstrated a significant variation in yield between detection methods and a high degree of variability in analytical results. Statistical analysis indicated the analytical variance of measurements between laboratories was a function of concentration and became more significant as the test concentration decreased. The freon extraction-gravimetric detection method was selected for use in this investigation because the results are comparable to most other oil and grease data presented in the technical literature and to regulatory requirements.

37. Analysis of the results of the field and bench-scale studies revealed that in the concentration range evaluated (0 to 20 mg/l), the precision of the freon extraction-gravimetric detection method is essentially independent of concentration. Data from the bench-scale studies showed a slightly higher degree of variation than did field study data, and this could be expected due to the greater number of manipulative steps, each with inherent variability, used in the bench-scale studies.

38. Consideration of the limitations of analytical methods is important in evaluation of the results of the field sampling efforts and bench-scale studies discussed in subsequent parts of this report.

PART III: TREATMENT METHODS

39. Two approaches appear practical to reduce or minimize the oil and grease content of containment area return waters. One is to treat the return water before it is released to the receiving water. This is also termed "end-of-pipe" treatment and involves treatment at the disposal site. The other alternative is to minimize oil releases from dredged material during slurry transportation by addition of materials that adsorb oil from the water phase before the return water is discharged.

40. The following section is a review of the two treatment alternatives and an evaluation of each process in terms of feasibility to resolve any oil pollution problem that might be caused by maintenance dredging operations.

Potential End-of-pipe Treatment Methods

41. Return water from dredged material containment areas may contain free and/or emulsified oils, the quantity of each depending upon the dredging technique employed. The term "free oils" refers to those oily substances that are immiscible in water and tend to separate from the aqueous phase due to the action of gravitational forces. Emulsified oils are those materials that form emulsions in water, that are finely dispersed, and that are composed of extremely small globules not separable from the water by gravitational forces. Emulsions are formed by reactions between the oily materials and other substances, such as finely divided inorganic solids or soaps, which change the electrical charge on the globules and prevent agglomeration and separation of the oils from the aqueous phase. Soluble oils are those oils that are completely miscible in water. In the case of hydraulic dredging, considerable amounts of oil may be in the emulsified state due to the high shearing forces associated with pumping. Soluble oils present in sediments, in equilibrium with the overlying water or interstitial water, may diffuse into the water from the sediments or vice versa. Insoluble

oils present in the sediment are usually trapped or coated on sediment solids. They may be released to the water during the process of dredging or slurry transportation and could remain in the return water unless removed by treatment.

42. The following discussion is intended to serve as a brief review of treatment methods for the removal of oil and grease from wastewaters. Processes for removing oil from wastewater can be classified into three categories: primary gravity separation, secondary deoiling, and tertiary polishing. The most commonly employed processes are shown in Figure 8. The design and operational characteristics of each of these unit processes are such that they have potential applicability to the treatment of return flows from containment areas. The primary advantages and disadvantages of these oil removal processes are summarized in Table 6.

Gravity separation

43. Gravity separation to remove oil is usually the first process step in the treatment of oily wastewater. Gravity-type separators depend upon the difference in specific gravity of oil and water. Oil separators usually are designed according to American Petroleum Institute (API) specifications to remove droplets larger than 150 μ in diameter.

44. Gravity separation is usually accomplished through the use of the standard API oil separator. This device may be a rectangular tank with oil skimming equipment, a parallel plate interceptor (PPI), or a corrugated plate interceptor (CPI). The PPI and CPI facilities are modifications of the standard API separator in that plates are set at an angle in the tank to decrease the overflow rate and enhance oil separation. As the wastewater flows between the plates, the oil droplets float upward and adhere to the plates. They subsequently coalesce into large droplets and rise to the surface.

45. Gravity separators are effective in removing considerable amounts of free oil and some emulsified oil. However, soluble oil and a large portion of the emulsified oil will remain in the separator effluent. The effluents from these treatment devices, when operated properly, may contain 30 to 150 mg/l of oil in a typical oily wastewater.

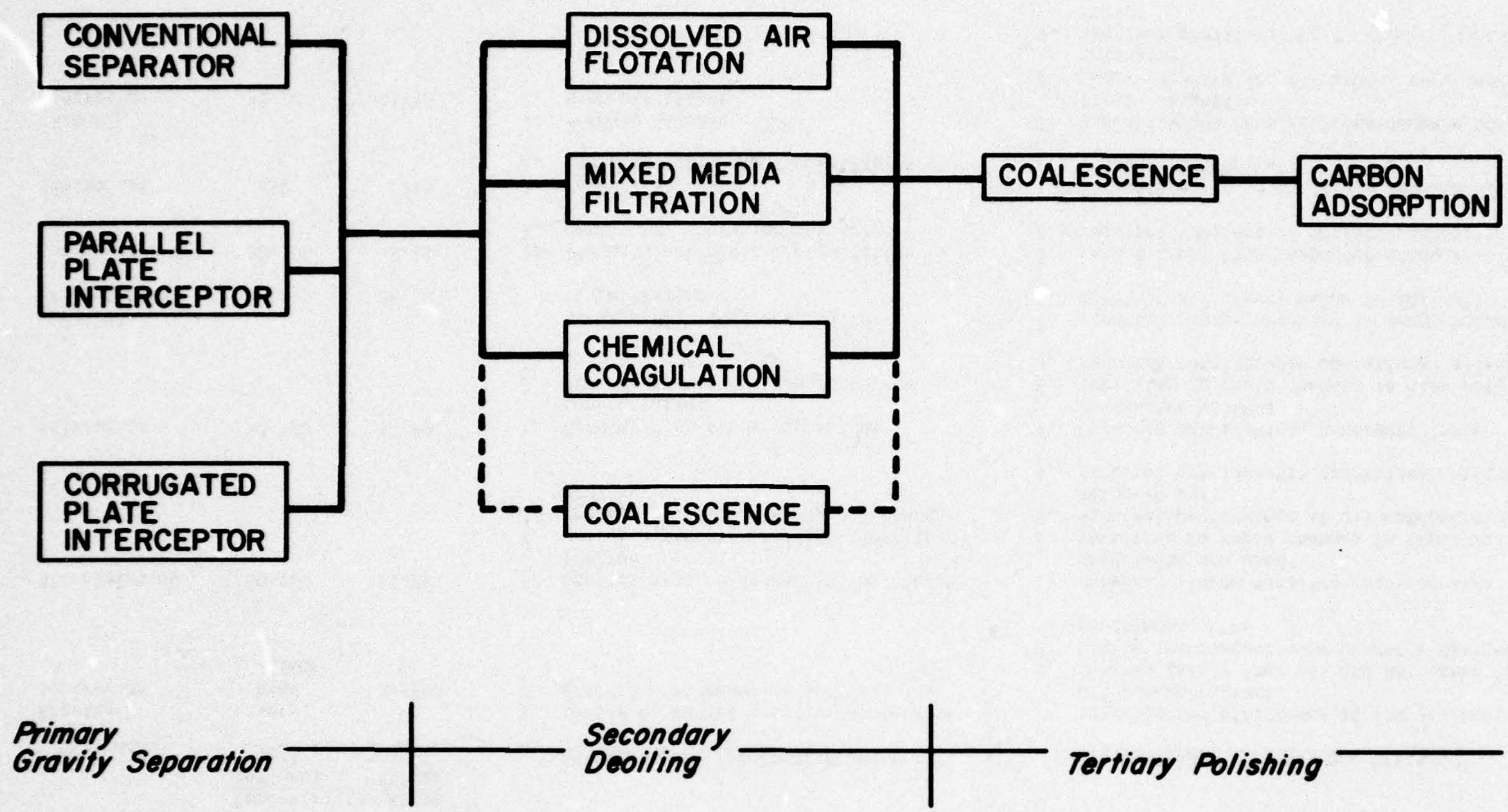

Figure 8. Current Physical-Chemical Treatment Methods for Oily Wastes

Table 6

Oil Removal Processes Comparison

Process	Effective Oil & Grease Concentration Range: Influent mg/l	Effective Oil & Grease Concentration Range: Effluent mg/l	Advantages of Treatment Process	Disadvantages of Treatment Process
Gravity Separation	very high >1000	30-150	1. simple operation and low maintenance 2. effective in removing solids	1. very limited efficiency at low influent oil concentrations 2. removes mainly free oil and not other forms 3. little improvement over properly designed containment area
Air Flotation	50-150	15-25	1. handles high suspended solids concentration 2. reliable process (handles shock load) 3. treats to reasonably low oil concentration	1. chemical sludge handling required when coagulants are used 2. sensitive to rapid changes in flow rate 3. marginal performance at oil concentration below 25 mg/l 4. requires considerable operational attention
Filtration	50-150	10-20	1. handles high suspended solids concentration 2. low attainable oil concentration	1. requires backwashing; generates large wastewater volumes 2. sensitive to rapid changes in flow rate 3. requires considerable operational attention
Chemical Flocculation	300	25-50	1. handles high suspended solids concentration	1. chemical sludge produced in large volumes 2. marginal efficiency below 50 mg/l oil
Coalescence	30-100	<5-15	1. low attainable oil concentration 2. continuous operation possible	1. cannot treat high suspended concentrations 2. requires substantial operator attention
Biological	<50	5-15	1. removes soluble oil 2. low attainable oil concentration	1. infeasible for return flows because of low organics concentration
Carbon Adsorption	10-20	<1-10	1. removes soluble oil 2. high efficiency	1. expensive and requires considerable operational attention 2. needs regeneration of carbon, very energy intensive 3. requires prefiltration to remove suspended solids

Although primary gravity separation will not provide a satisfactory quality effluent for direct discharge, it is the most economical and efficient way to remove large portions of free oil.

46. Since it is expected that return waters will generally contain concentrations of free oil less than 50 mg/l, gravity separation is not considered a feasible method for treating containment area effluents.

Dissolved air flotation

47. Dissolved air flotation (DAF) is a commonly accepted practice in the petroleum refining industry for the supplemental treatment of gravity separator effluents. In this process, the entire wastewater stream or some fraction thereof is saturated under pressure with a gas, usually air. Upon release of this pressure, the air in excess of the atmospheric saturation concentration is released from solution, forming bubbles approximately 30 to 120 μ in diameter. The bubbles form on the surfaces of suspended and oily materials, or are attached to the particles by surface energy. Thus, an aggregate, whose average density is less than that of water, is formed and will rise to the surface.

48. Dissolved air flotation can be used by itself, but for maximum effectiveness it is used with chemical coagulation and flocculation. The chemical treatment aspects of DAF operation are extremely important, particularly when soluble, colloidal, or emulsified oil components are present. Coagulants such as lime, alum, ferric salts, or polyelectrolytes are used to improve floc formation and provide good separation. They can be injected at several points depending on the flotation process and the chemical used. In some installations, the chemical is injected downstream of the pressure relief valve, while in others it is injected into the pressurizing pump station.

49. The removal of oil in DAF units can be documented by referring to case histories where pressurized DAF units are used to treat refinery oily wastewaters.[11] Based on wastewater surveys within refineries having DAF units, statistical analyses of DAF process efficiency were made when sufficient data were available. Data for the first case history, in which a rectangular DAF unit has been in operation in series

with an API separator for several years, are graphically presented in Figure 9. As noted, the DAF unit reduces the total oil from 68 mg/l to 15 mg/l at a 50 percent probability and from 105 mg/l to 26 mg/l at a 90 percent probability.

50. Additional DAF oil and grease data for units treating oil and gas production wastes are plotted in Figure 10.[12] In this analysis, data were grouped and an average removal efficiency was used in each group for graphical presentation. Limited data were reported for low influent oil concentrations, and it is doubtful that the removal efficiency will be as high as shown in Figure 10 in the low influent oil range.

51. An alternate system to DAF is induced air flotation (IAF). In this system, air is dispersed in the liquid phase by specially designed turbine mixers or inducers. Usually, a unit operates with four mixers in a series of bays. The mixer operation is intermittent: air is dispersed during mixing; the mixer is shut off for the float to form; the float is skimmed from the unit; and the treated water is discharged to the next cell. The process is then repeated. Polyelectrolytes for emulsion breaking are a necessity for IAF unit operation. An advantage of IAF units is that they are modular and can be moved as a unit from one site to another.

52. Summarizing, air flotation with chemical treatment is a viable oil removal method if return flow oil and grease concentrations are in the range from 25 to 50 mg/l. Performance at concentrations below 20 mg/l can be expected to be erratic and a probable limit of treatment capability of the units, on an average basis, is a 15-mg/l effluent oil and grease concentration.

Filtration

53. Filtration systems have been recently applied to the separation of free and emulsified oil from wastewater streams. A broad spectrum of materials, including glass, porous ceramic, metals, plastics, sand, anthracite, and graphite have been tested as filter media. The oil removal mechanism is by direct filtration and induced coalescence. The majority of oily waste streams will contain some amount of fine

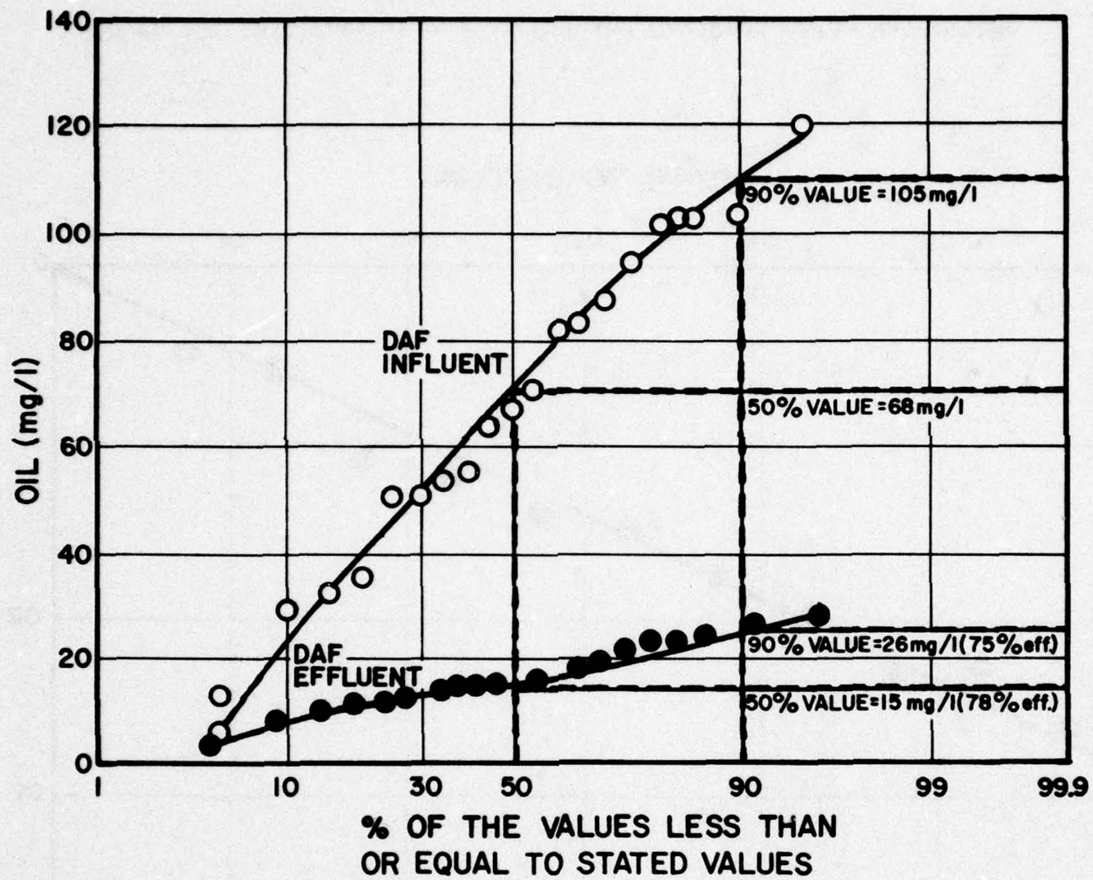

Figure 9. DAF Oil Removal Performance

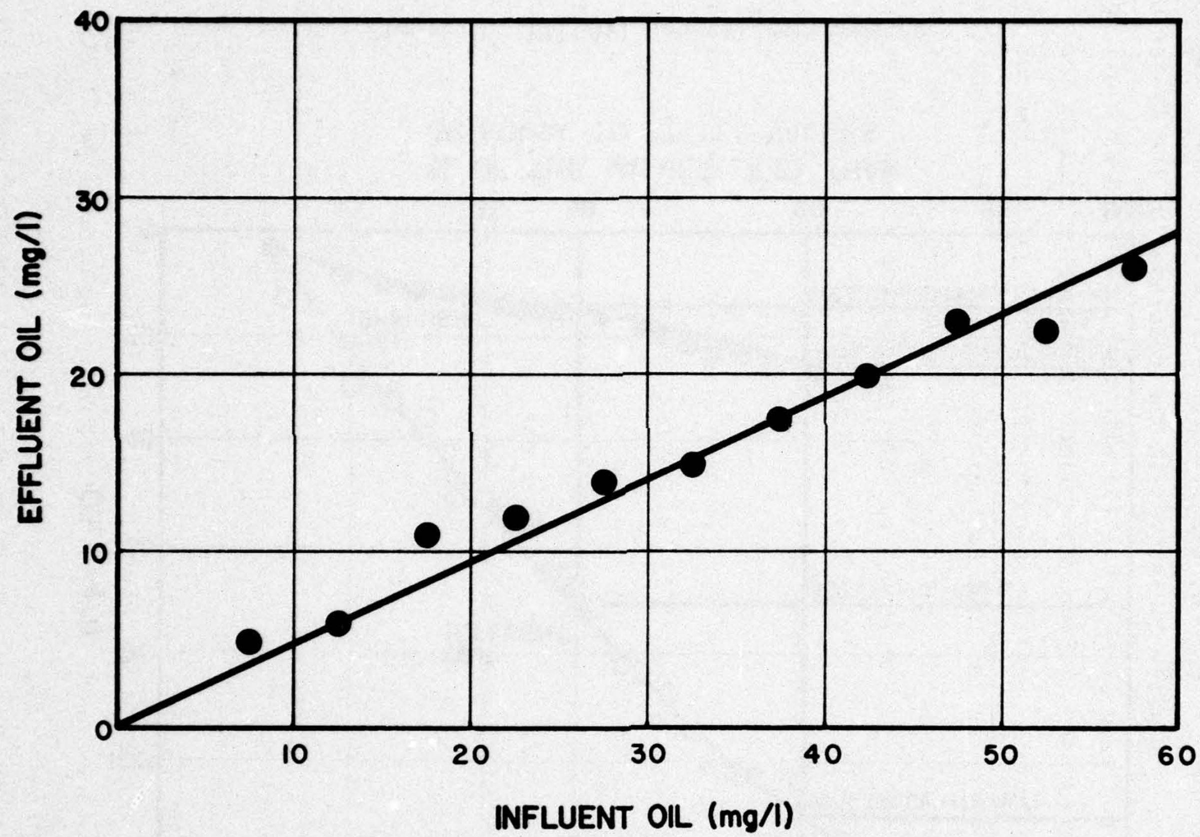

Figure 10. DAF Performance on Oil and Gas Production Wastewater

solids and, this is particularly true for dredged material. These solid particles tend to remain on the oil/water interface and form a loose structure around the oil globules inhibiting coalescence. As the wastewater flows through the filter, depositing its solids in the top few centimeters of the filter bed, the oil droplets, without their combined solids, will more readily coalesce. In the remainder of the filter bed, oil droplets coalesce as they collide with each other and with oil-wet surfaces. Coalesced oil tends to collect in the upper part of the filter and may not accumulate in sufficient quantities to flow out with the filtered water by the time backwashing is needed. The effectiveness of the filtration process in resolving emulsions is probably due to the rupturing of the oil globules on passage through the filter medium, allowing these particles to coalesce into separate phases.

54. Potential advantages of filtration in treating oily wastes include reduction of the free oil content to values approaching 10 mg/l, removal of oily solids, and construction and operating costs substantially less than the cost of a gravity separation system designed to reach the same effluent oil concentration.

55. A filter column containing 1.68 m of sand, 0.76 m of graded anthracite coal, and 0.41 m of gravel was used to treat API separator effluent. The oil concentration in the influent ranged from 35 to 178 mg/l, and the effluent contained from 7 to 17 mg/l with an average of 11 mg/l oil. Addition of coagulant (1 to 5 mg/l) did not improve performance.[13]

56. Actual operational data from the system designed from the previously mentioned pilot study were compiled. The results are plotted in Figure 11 for comparison. Since it is anticipated that the total oil content in any return water will not exceed 70 mg/l, data with oil in excess of 70 mg/l were not used in this analysis. Again, oil removal efficiency in the lower range is questionable because of the limited data available.

57. Multimedia, high-rate filtration has been employed to treat oily wastewater. The filter system effectively intercepts 90 to 95 percent of the free oils and some emulsified oils.[14] Dual-media

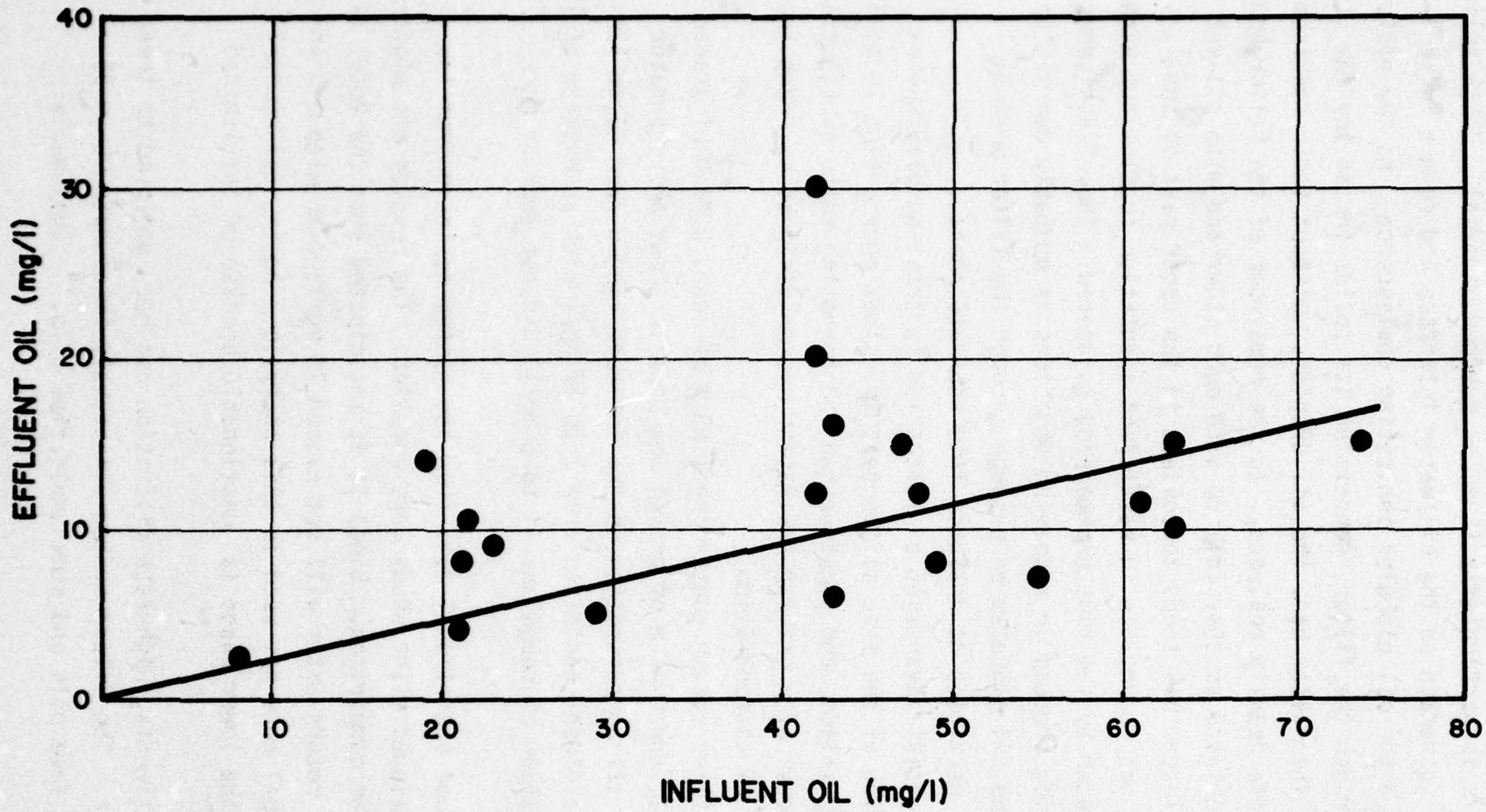

Figure 11. Oil Removed by Sand Filtration

filtration as a final step in the treatment of oily wastes before injection to the groundwater system was investigated. Reported oil removal efficiency averaged 77 percent with a range of 66 to 86 percent.[15]

58. Humenick et al.[16] investigated separation of solid-stabilized oil emulsions in a filter bed having a total depth of 1.8 m with equal amounts of graded anthracite coal and sand. Oil concentrations ranged from 100 to 500 mg/l, and the filtration rates varied from 3.4×10^{-3} to 1.02×10^{-2} m^3/m^2-sec. They concluded that without chemical filter aids this process was not practical. Addition of cationic polyelectrolytes resulted in better filter performance than did the addition of anionic or nonionic polyelectrolytes. It was reported that solid oil emulsion droplets remained intact whether the oily material was removed or passed through the filter bed. This observation disagrees with Beavon's hypothesis that oil and solid particles are separated in the filter.[17]

59. Higher oil-bearing capacities were found when crushed graphite ore was used instead of sand media. It was reported that 25 percent more oil adsorption was obtained with graphite ore rather than sand media. Better oil removals are believed to be due to the irregular particle shape and preferential sorption on the oil-wet graphite surface.[18]

60. Rotary vacuum precoat filters (diatomaceous earth) are commonly used when emulsions are stabilized by finely divided solids. The breaking of the emulsion occurs as a result of rupturing the globules in the dispersed phase when passing through the interstices of the filter cake and precoat material and as a result of removing the stabilizing solids. Ninety-nine percent removal of oil and grease was obtained when a precoat filter and an air flotation unit were used to remove grease and tallow from poultry and livestock processing wastes.[19] However, precoat filters have been used to a limited extent to remove oil from oily wastewater. Large capital investment and high operating costs, as well as the filter cake disposal requirement, render the economics of the process unfavorable. This is particularly true when large volumes of water must be treated at high flow rates, which would be the case with return waters from maintenance dredging operations.

61. Hay filters are generally regarded as being relatively inexpensive but not very effective. Their effectiveness depends on the quantity and character of the oil to be removed and the frequency with which the filter medium is replaced. A hay filter performs two functions: it removes suspended matter by filtration and oil by adsorption. As the filter becomes saturated, adsorption ceases, the filter starts to act as a coalescer, and oil begins to pass through the filter. At this point, the medium must be removed. The required frequency of removal may make this process impractical depending upon the application.[20]

Chemical coagulation

62. This process includes the addition of chemical coagulants to produce microflocs. Coagulation and the flocculation of these small particles allow their removal by sedimentation. Use of variable amounts of sulfuric acid, aluminum sulfate, and a nonionic polyelectrolyte for flocculation of alkaline oily materials has been practiced. The raw waste contained 300 mg/l of oil and grease, which was reduced to 28 mg/l in the treated effluent.[21] For water-soluble oils, sodium carbonate and lime are added prior to regular treatment.

63. Ferric chloride solution is used as coagulant for an industrial waste containing approximately 800 mg/l oil. After settling and separating the sludge oil, sulfuric acid is added to release the ferric chloride for recycling. The treated water contains approximately 25 mg/l of oil.[22] In a separate study, an emulsion containing water-soluble cutting oil was treated with ferric chloride to break the emulsion, flocculated with aqueous calcium carbonate, and mixed with polymeric flocculant to produce a firm precipitate. The supernatant was removed by filtration and discharged. An influent with 10,000 mg/l oil was reduced to less than 10 mg/l oil in the treated effluent.[23]

64. The combination of flocculation and filtration is also practiced. In an attempt to remove solid-stabilized oil emulsion in a 1.83-m filter column containing sand and graded anthracite coal, the addition of polyelectrolyte was found to improve the performance significantly.[16]

65. Upflow clarifiers have been used in lieu of the conventional flocculation-sedimentation system with chemical addition. In an upflow clarifier, the floc formed is removed in the sludge blanket as the water flows upward. Chemicals such as lime, alum, and polyelectrolytes are added before the wastewater enters the clarifier. Effluent oil concentrations as low as 10 mg/l have been reported.[24]

Coalescence

66. Recently, coalescence has been applied to wastewater treatment to remove the residual secondary oil-water emulsions that are not separable under prolonged detention in gravity separators. Fibrous-bed coalescers generally have a fixed filter element constructed of fiberglass or other materials that act to coalesce the oil droplets and break emulsions. The coalesced oil droplets released from the filter are readily separated downstream by gravity. Coalescence in a fibrous-bed coalescer involves three steps: (1) interception of fine droplets by fibers; (2) attachment of droplets to the fibers or on retained droplets; and (3) release of enlarged droplets from the fibers.

67. Demulsification by induced coalescence is due to the rupture of the protecting film when the emulsion flows through the small passages in the fibrous media and the subsequent coalescing of the dispersed phase due to the preferential wetting characteristics of the media surface. Reported data[12] on fibrous coalescer performance were compiled and plotted in Figure 12. Again, these data were grouped and average values were used for the presentation. Approximately 60 percent removal can be expected within the influent oil range studied.

68. Artificial oil dispersions and actual wastewaters were tested in a 0.093-m^2 coalescer using commercial glass fibers 3.2 μ in diameter coated with phenol-formaldehyde resin; the oil removal was nearly 100 percent at the 5.09×10^{-3} m^3/m^2-sec filtration rate. The oil content was reduced from influent concentrations ranging from 10 to 85 mg/l to effluent concentrations of 3 mg/l or less.[25] API skimmings and coker slop oils from a typical refinery were used to determine the coalescer performance in a laboratory-scale study. Oil removals of greater than 85 percent were obtained when 0.0127-m polyester felt was used as the

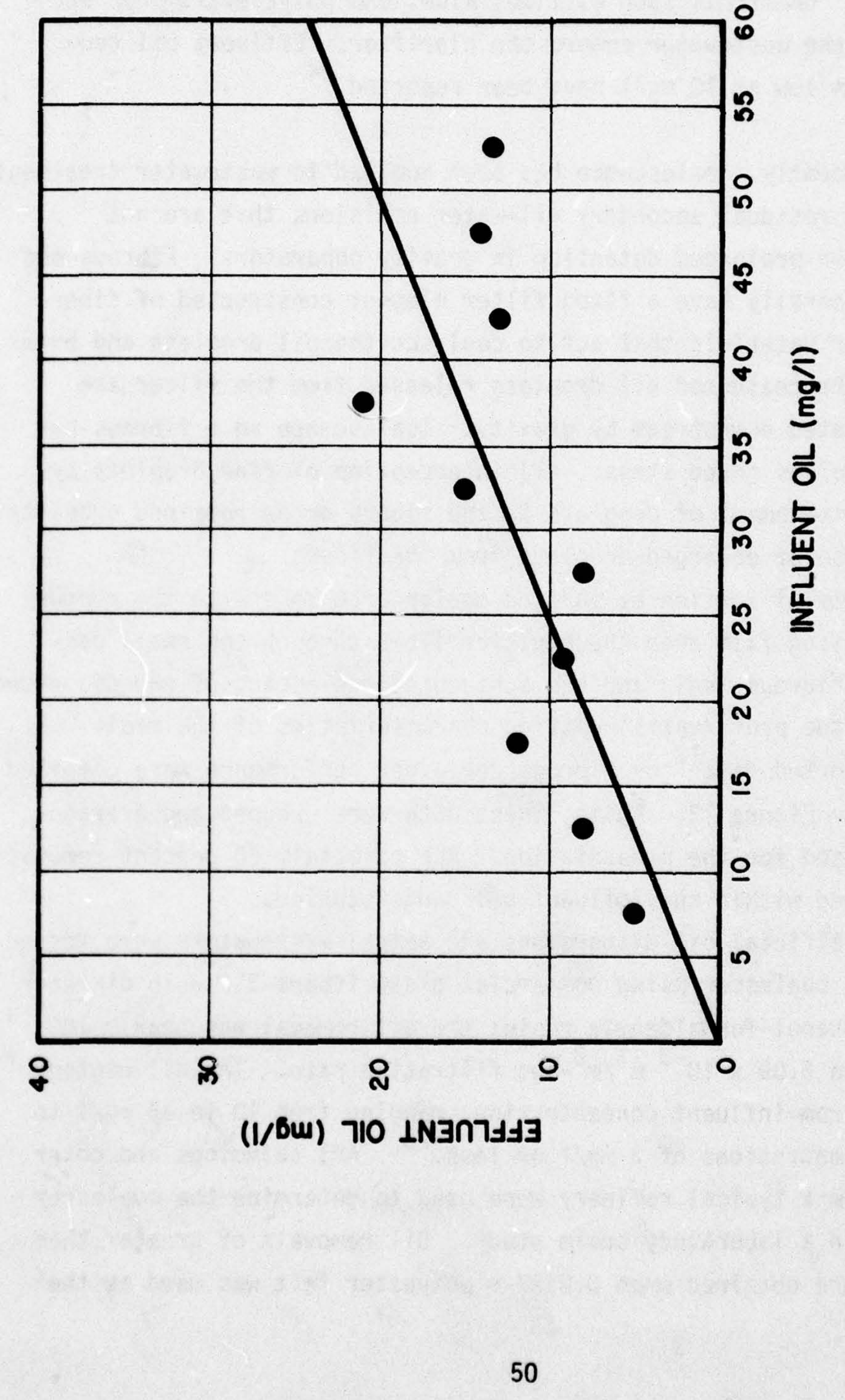

Figure 12. Oil Removed by Fibrous Coalescer

coalescing medium at a filtration rate of 6.79×10^{-3} m^3/m^2-sec. Influent oil concentrations ranged from 100 to 300 mg/l.[26] It was found that a steady-state oil removal can be achieved after the fibrous beds are saturated with dispersed oil. Continuous operation is possible before excessive pressure drops are reached. A major shortcoming of fibrous coalescers treating emulsified wastes is the relative inability of these coalescers to treat waste streams containing significant concentrations of suspended solids.

Biological processes

69. Biological treatment processes have limited ability to remove oil. While biological processes are efficient in oxidizing soluble organic compounds including some soluble oils, the amount of free and emulsified oil that may be applied to biological treatment processes is limited. Free oil coats the biological floc and inhibits efficient oxygen and substrate transfer within the biomass. Emulsified oil has also been observed to be "broken" in biological reactors causing the same problem indicated above for free oil. Excessive amounts of oily materials interfere with the performance of activated sludge systems. The accumulation of oils on sludge causes a loss of density and consequently sludge carries over the effluent weir, causing higher total suspended solids and associated oil and grease levels in the effluent.

70. Use of activated sludge and dried bacterial cultures (a species of saprophytic bacteria that consumes oils) to reduce effluent waste loads at a bulk oil handling terminal was reported. The system was used to treat a variety of waste oils and included a collection system, an API separator, high-rate biological oxidation, and secondary sedimentation.[27] A final efficiency of 97-percent waste load reduction was reported with the application of this system.

Carbon adsorption

71. Activated carbon adsorption has very limited use in the removal of oil. Adsorption primarily removes soluble oil. In addition, wastewater applied to activated carbon adsorption units must be pretreated to a high degree to prevent clogging and coating of the activated carbon. If the activated carbon adsorption units are not

adequately protected from clogging, the units will have to be frequently backwashed and the activated carbon possibly regenerated or replaced.

72. Carbon adsorption was used to treat sand filter effluent on a pilot scale.[13] Four columns were used in series. The first column was 0.91 m deep and each of the remaining columns were 1.52 m deep, with a filtration rate of 2.44×10^{-3} m^3/m^2-sec. Influent oil concentrations ranged from 7.5 to 17.2 mg/l, while the effluent oil concentrations ranged from 0.8 to 2.5 mg/l. However, operational data of the prototype plant designed on the basis of these pilot-plant data revealed an average effluent oil concentration of approximately 9.0 mg/l, with maximum concentrations greater than 25 mg/l. Average influent oil concentration to the carbon column was 35 mg/l, resulting in an average 74 percent removal efficiency. Operating data from this prototype plant are plotted in Figure 13.[28]

Summary

73. A description of different processes applied to the removal of wastewater oil and grease has been presented. Few of these processes appear applicable to return flows because of the relatively low influent oil and grease concentrations expected. Those unit processes with the highest potential applicability to return flows include granular-media filtration and coalescence.

Sediment Treatment Methods

74. One way to resolve potential oil and grease problems in return waters from dredged material containment areas is to minimize the release of oily substances from the dredged material. This objective may be achieved in two ways: (1) maximize the sorptive capacity of the dredged material for oil and grease and/or (2) add materials with high sorptive capacity to the sediments to increase the overall sorptive capacity of the solids in the dredged slurry.

75. This section will include a brief review of sorption theory, the potential addition of oil adsorptive materials to dredged sediments, and some concepts on adhesion and wetting of oil on solid surfaces.

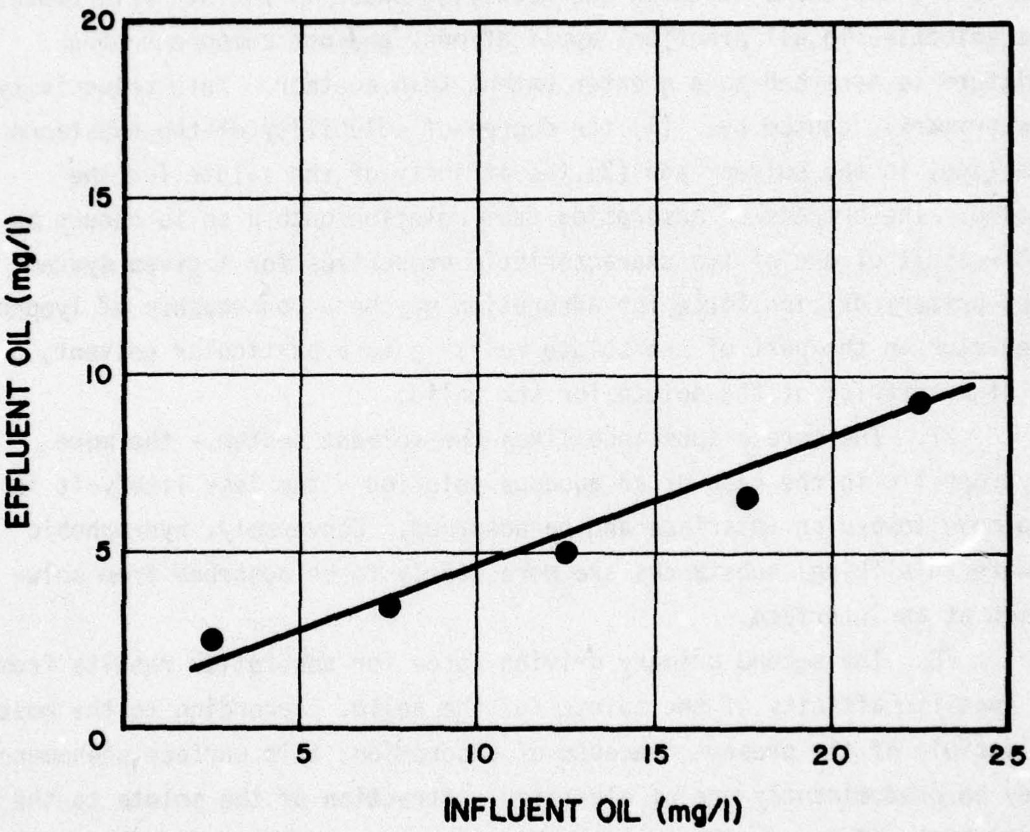

Figure 13. Oil Removed by Carbon Adsorption

Other pertinent information on sorption theory with respect to oily substances will also be discussed.

Sorption theory

76. The term "sorption" is a very general expression for a process in which a component moves from one phase to another, particularly for the cases in which the receiving phase is solid. This process is selective in all practical applications, and one component of a mixture is adsorbed to a greater extent than another. This selectivity is primarily caused by: (1) the degree of solubility of the substance (solute) in the solvent and (2) the affinity of the solute for the solid. The process of adsorption from solution onto a solid occurs as the result of one of two characteristic properties for a given system. The primary driving force for adsorption may be a consequence of lyophobic behavior on the part of the solute relative to a particular solvent, or a high affinity of the solute for the solid.

77. The more a substance likes the solvent system - the more hydrophylic in the case of an aqueous solution - the less likely it is to move toward an interface and be adsorbed. Conversely, hydrophobic (water-disliking) substances are more likely to be adsorbed from solution at an interface.

78. The second primary driving force for adsorption results from a specific affinity of the solute for the solid. According to the most plausible of the present concepts of adsorption, this surface phenomenon may be predominantly one of electrical attraction of the solute to the adsorbent, of Van der Waals attraction, or of a chemical nature.

79. Some of the influencing factors on adsorption of a solute on a solid are reviewed by Weber.[29] These are: (1) surface area, (2) concentration of solute, (3) nature of adsorbate, (4) pH, (5) temperature, and (6) nature of absorbent. In order for adsorption to occur, it is necessary that a compound have some type of polar group. These polar groups are attached to the adsorbent by chemical interaction at the surface between the functional groups. It is recognized that oil adsorption by sediments and by other additives such as activated carbon can be of significantly different degrees due to different surface properties of the adsorbents.

Adhesion

80. There are mechanisms for oil accumulation in sediments other than adsorption. Water and oil in free and emulsified forms are mutually immiscible. Therefore, adsorption between solute-solvent and solid systems may not explain excessive oil accumulations in the sediments. Emulsified and free oil in sediments may originate from industrial or municipal wastewater discharge where oils coat or adhere to suspended solids. These oil-coated solids finally settle out in the bottom sediments. It is reasonable to assume that these oils are most likely to be released from the sediment during dredging operations.

81. The addition of a surfactant (wetting agent) may increase the sorptive capacity of dredged material. The surfactant is adsorbed at the solid-liquid and liquid-liquid interfaces and lowers interfacial tension. In a practical sense relative to the oil-sediment problem, the degree of adhesion of an oil to sediment particles is primarily a function of characteristics of the given oil. Since a wide variety of oils can be expected in natural waters, the degree of adhesion of the oil and the solids probably varies significantly. It appears impractical to consider using any type of additive to increase adhesion of oil to sediments; in fact, due to their dispersing action, surfactants might be detrimental since their effect would be to emulsify any free oil contained in the waters associated with the dredged sediments.

Current treatment practice

82. As mentioned previously, one way to reduce oil release is by addition of highly adsorptive substances to the dredged slurry. One of the materials most commonly employed to adsorb contaminants from wastewater is activated carbon. Granular and powdered activated carbon have been used extensively in wastewater treatment. Application of granular activated carbon in a column has been discussed in the previous section. Therefore, only the powdered carbon application will be discussed here. Other adsorbents such as graphite, coal, and coke have also been used to adsorb oil from wastewater with various levels of success.

83. Addition of powdered activated carbon in wastewater treatment to upgrade performance has been practiced. Most of these cases are associated with the addition of powdered carbon in the aeration tank of

an activated sludge process. Improved organics removal, reduced foaming, and better sludge settling have been found. However, no data have been found relating the application of the powdered activated carbon to oil removal.

84. Hydrophobic Teflon powders have been used to adsorb oil from water. The treated water contained oil in the range of 100 mg/l to trace amounts. After addition of the polymer, the powder was thoroughly stirred and filtered. The spent polymer could be regenerated with an organic solvent and reused. The smaller the particles, the more effective was the oil removal.[30]

85. In a separate study, oil was removed from wastewater by dispersing graphite oxide and a coagulant into oil-containing water and separating the resulting precipitates. Thus, three ml of machine oil were emulsified in one l of water to obtain the resulting oil emulsion containing 5,700 ppm of oil. To this emulsion 100 ppm of graphite and 240 ppm of aluminum sulfate [$Al_2(SO_4)_3$] were added. After agitating, the mixture was filtered to obtain water having a total oil content of 110 mg/l.[31]

86. Tamaki et al.[32] described a process for removing oils from aqueous waste. The process consists of the following steps: (1) addition of oil-adsorbing material; (2) aeration of the solution; and (3) removal of the resultant foams that contain the oils adsorbed in the adsorbent. Thus, 500 ppm of coal powder (particle size less than or equal to 5×10^{-4} m) was added to a waste solution containing 50 mg/l roller oil; the solution was then aerated one min in a mechanical stirring type aerator, and the foams were removed to give treated water containing 0.4 mg/l of oil. Powders of cokes and blast furnace slags were also used successfully instead of the coal powder.

87. In a recent study, 93 compounds commonly found in petrochemical waste streams were used to evaluate adsorbability on activated carbon. It was found that adsorbability by activated carbon increases as the molecular weight and chemical structual branching increase and polarity and solubility decrease.[33]

Natural decomposition

88. Oils in sediments are decomposed biologically under both aerobic and anaerobic conditions. Since some of the oil components are rather complex, the bacteria may only decompose the simplest oil components.

89. A recent study on aerobic decomposition of oil pollutants in sediments showed a 4.5 percent loss of oils from sediments during the 33-week study period.[34] Experimental results strongly illustrated that oils that reach the bottom sediments of rivers and other water bodies are markedly changed from crude petroleum. No compounds having a boiling point below 220°C were present in the sediment studies. This corresponds to a straight-chained alkane with a chain length of approximately 20 carbon atoms, implying that those compounds in the sediment are larger molecules than this.

90. Loss of oils from polluted bottom sediments has also been reported by Vorashilova and Dianova[35] in studies of the Moscow River. They reported a cyclic migration of oil from the surface to the bottom sediment and back to the surface. The authors also reported that soluble decomposition products were released to the overlying water. The amount of oil evolved in the summer ranged from 0.006 to 0.017 kg/m^2-day.

91. Brown,[36] studying the decomposition products of petroleum in natural waters, found that the microflora caused marked physical changes in oil. He demonstrated that chemical changes occurred in the oil during microbial decomposition and that certain fractions of oil were changed in polarity and/or molecular weight.

92. Blumer et al.[37] showed a general decrease over time of the presence of the low molecular weight hydrocarbons in oil removed from the sediment. These hydrocarbons are more readily soluble and would be dissolved when in contact with water for an appreciable length of time. He stated further that greater volatility of the low boiling normal alkanes is also an important factor in their loss. These hydrocarbons were also found to be the most immediately toxic fraction of the oil and responsible for the lethal effect of the oil on the fauna.

93. Shelton and Hunter[38] studied anaerobic decomposition of oil in sediments. They found that oil loss in sediment by anaerobic bacterial decomposition is greater than that obtained under aerobic conditions. Also, oils were more readily lost than other organic matter present. It was postulated that an increase in solubility and diffusion as a result of some biochemical alteration rather than actual biochemical decomposition was responsible for the rapid loss. There is no observable change in the benzene-extractable compounds in a natural bottom sediment containing oil under anaerobic conditions.

Summary

94. This part included a short review of sorption theory and some treatment practices involving addition of adsorptive materials to separate oil from wastewaters. In general, the treatment involves addition of powdered materials or coagulants. Oils are adsorbed onto the slurry and are separated before the treated effluents are discharged.

95. Activated carbon, Teflon, coal, and slag provide reasonable oil removal efficiency. However, since these oil adsorbents are disposed with the dredged material and not recycled, the cost associated with this treatment may be prohibitive. The mechanism of oil sorption onto the additives mentioned above is identical, whether the oils are adsorbed onto a slurry or in a column consisting of highly adsorptive material.

PART IV: FIELD SURVEY

96. This part describes the procedures and the results of field surveys assessing potential oil and grease contamination of surface waters from dredging operations. Background information on the field sampling locations is presented. Sampling and analytical techniques are also discussed.

Site Selection

97. Sampling sites were selected based on the following considerations: (1) type of aquatic environment (river and estuary should each be represented); (2) major waste discharges (industrial and municipal wastes should both be represented); and (3) dredged material containment areas should be in use (if possible). Four Districts of the Corps of Engineers were selected: Buffalo, Galveston, Detroit, and Savannah. The sampling sites selected in these Districts are as follows: (1) Buffalo - Cuyahoga River; (2) Galveston - Houston Ship Channel, Texas City Channel, Sabine-Neches Canal; (3) Detroit - Rouge River; and (4) Savannah - Brunswick Harbor.

98. Two river and four estuary sites were selected. The study sites are near major urban centers and industries known to discharge significant quantities of oil (e.g., the petroleum refining and steel industries). The site selection was based on an evaluation of water-quality and sediment data provided by the respective Corps of Engineers District Offices. These data reveal that large quantities of oil are present in some of the sediments at these dredging sites. Although there is currently no proof that the amount of oil in the sediments is related to the amount of oil released during dredging, it is likely that more oil will be found in the return waters from dredged sediments containing high concentrations of oil.

99. Two river sites were selected in the Great Lakes area, these being the Cuyahoga River in Cleveland and the Rouge River in Detroit. The major industries along the Cuyahoga River manufacture steel and

related products. The Rouge River was selected because of the wastewater discharges and the heavy industrial development, including the large automobile manufacturing plants, which are located along its course.

100. The three sites selected in the Galveston District are highly industrialized. Refineries and petrochemical plants are among the dischargers to these waters. Although sediment data from the Corps of Engineers and the Texas Water Quality Board (TWQB) do not show excessive quantities of oil and grease compared with the river sites selected, these sites were chosen because of their proximity to major hydrocarbon discharges, as well as the availability of supporting water-quality data from the TWQB.

101. Data from the Savannah District indicate that as high as 10 percent by dry weight of sediment samples taken from a virgin dredging site in Brunswick Harbor is oil and grease. Even in regularly maintained areas, sediment oil and grease has been found to exceed three percent by weight. Municipalities and industries, including a chemical plant and a pulp and paper mill, discharge wastewater to this body of water.

102. The sampling sites represent a wide range of conditions and provide a good basis, under the scope of this project, for determination of the extent of oil and grease problems related to dredging.

Background Information

103. In order to assist in evaluating the results of this study, it is necessary to present pertinent background information on the sampling sites. This background information includes quantities of oil and grease discharged in the vicinity of each dredging site, frequency of dredging, and dredging techniques employed. Oil and grease contributions may originate from industrial operations, municipal wastewater discharges, storm runoff from contaminated areas, or accidental spills. Effluent quality data for the wastewater discharges from industries and municipalities at each study site were collected from regulatory agencies.

In instances where these data were not available, effluent limitations from National Pollutant Discharge Elimination System (NPDES) Permits were obtained. Data from the Corps of Engineers' previous studies at these sites were gathered as supporting information.[39, 40, 41, 42] These data were used in selecting the study sites as well as sampling stations at each selected site.

Cuyahoga River - Cleveland

104. The Cuyahoga River receives continuous wastewater discharges from industries along the river. The major dischargers of oil and grease in the vicinity are the steel industries. Another possible source of oil is runoff from oil tank farms. These tank farms usually have no operations that discharge wastewater; however, surface runoff from the farm areas can contain significant quantities of oil. Since no self-reporting data are available for these industries, only the NPDES Permit limitations on oil discharges are presented. The location of the sampling stations as well as industries in the vicinity of the study site are shown in Figure 14. The levels of allowable oil discharge into the Cuyahoga River are tabulated in Table 7.

105. The dredging operation at the Cuyahoga River is contracted by the Great Lake Dredging Company. The dredging involves a bucket (clam shell type), which picks up the sediment from the river bottom and places it on a barge near the dredge. When the barge is filled, it is towed to the disposal site and the dredged material is pumped to a diked area.

106. Four sampling stations were selected to cover a broad range of sediment oil concentrations (Figure 14). At the time of this survey, the dredge was located at Station 1. Station 3 is located approximately six miles up the river, at the limit of the federal dredging operations. Station 4 is located at the intersection of the old Cuyahoga Channel and the new Channel.

107. Return water samples were collected from the dredged sediment on the barge at Stations 1 and 2. This involved collecting water that separated from the sediments in the barge itself. Since the dredged material is pumped from the barge to the diked area, oil may be

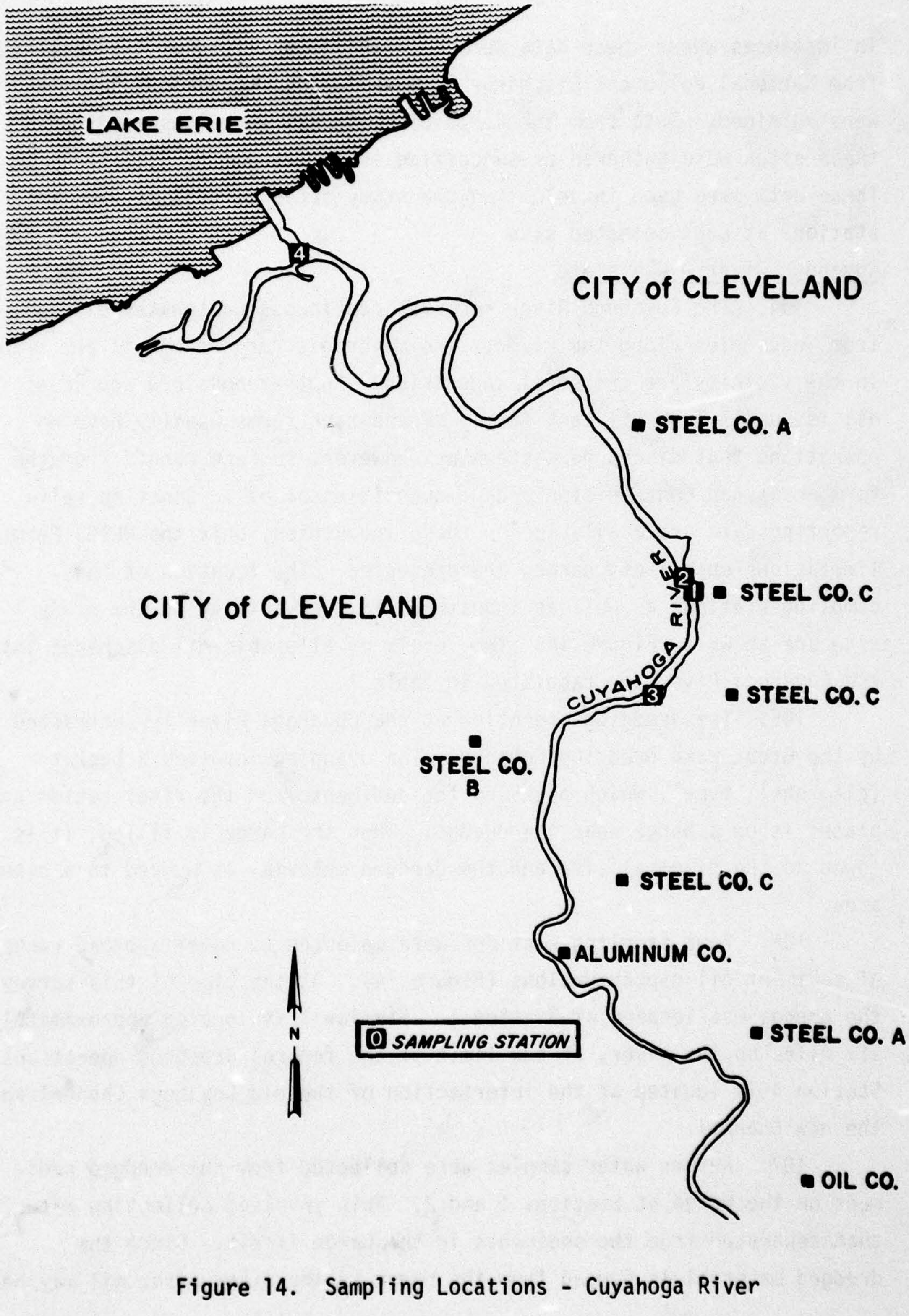

Figure 14. Sampling Locations - Cuyahoga River

Table 7

NPDES Permits on Oil Discharges in the Cuyahoga River Study Area

Industry	Outfall Location or Number	Monthly Average kg/day	Daily Maximum kg/day
Steel Company A	Broadway	-	5*
	E. 49th Street	-	5*
Steel Company B	001**	-	195
	002	-	211
	004**	804	1607
	007	-	795
Steel Company C	001	54*	258*
	005	-	-
	009	395	798
	011	881	2330
	014	-	-
	015	-	-
	601**	487	866
	602**	179	318
	604**	-	-
	605**	207	414
	606**	11	23

* Number expressed in mg/l; no flow requirements are specified.
** Storm runoff.

released from the slurry during transport as well as during the dredging process. In light of this possibility, spillway effluent at the diked disposal area was also sampled.

Rouge River - Detroit

108. The major industrial dischargers into the Rouge River include an automobile manufacturer, a chemicals manufacturer, a paper manufacturer, and several oil storage terminals. Contributions from each industry, in terms of oil quantities and concentrations, are tabulated in Table 8. These data were obtained from EPA's STORET system and cover a period of more than two years. As can be seen from Table 8, the major oil and grease discharger is the automobile manufacturer.

109. The dredge employed in the Rouge River is a hopper dredge. Dredged material is pumped twice in the operation of a hopper dredge. The dredged material is pumped into a container and then in turn pumped into a containment area when the container is full. Four sampling stations were selected at this site as indicated in Figure 15. All sampling stations were located near the Detroit River because the upper segment of the river had been dredged prior to the sampling trip.

Brunswick Harbor

110. There are only four point-source dischargers in the vicinity of Brunswick Harbor, including a chemical company, a power plant, a pulp and paper mill, and a waste treatment plant. The oil and grease discharges are quantified in Table 9. The location of the industries and the sampling stations at this site are shown in Figure 16. Four stations were selected based on the available water-quality data and the locations of the industries.

111. The fuel oil storage areas at the chemical company are diked. Pad runoff from these areas is treated with adsorbent prior to discharge. For oil pollution control in its waste treatment plant, the chemical company employs an oil boom, an adsorbent blanket or granules, or a portable belt-type oil skimmer, depending on the magnitude of the oil problem encountered.

Table 8

Oil and Grease in Industrial Discharges

Rouge River, Detroit

Industry	Flow m^3/sec	Oil and Grease Range mg/l	Oil and Grease Average mg/l	Oil and Grease Average kg/day	Source
Automobile Manufacturer	16.2	1-9	2.3	3197	-
Food Processor	8.80×10^{-3}	1-66	10.0	7.7	Tallow Grease
Oil Terminal A	-	1-6	4.0	-	Ballast Water
Cement Company	9.94×10^{-2}	-	5.0	43	-
Paper Company	5.90×10^{-2}	1-5	2.7	14	-
Chemical Company	1.56×10^{-2}	0.4-39.5	5.7	7.7	Chemical, Coal Tar
Chemical Company	2.00×10^{-2}	0.0-8.1	0.8	14	Coke, Coke Products
Oil Terminal B and Refinery	0-2.2	2-4.2	-	-	Terminal
Oil Terminal B and Refinery	3.96×10^{-2}	0.6-7.8	2.2	7.3	Process Water
Oil Refinery	4.40×10^{-4}	0.4-96	24.6	1	Compounding and Blending
Power Company	3.48×10^{-1}	1-2	1.5	45	-

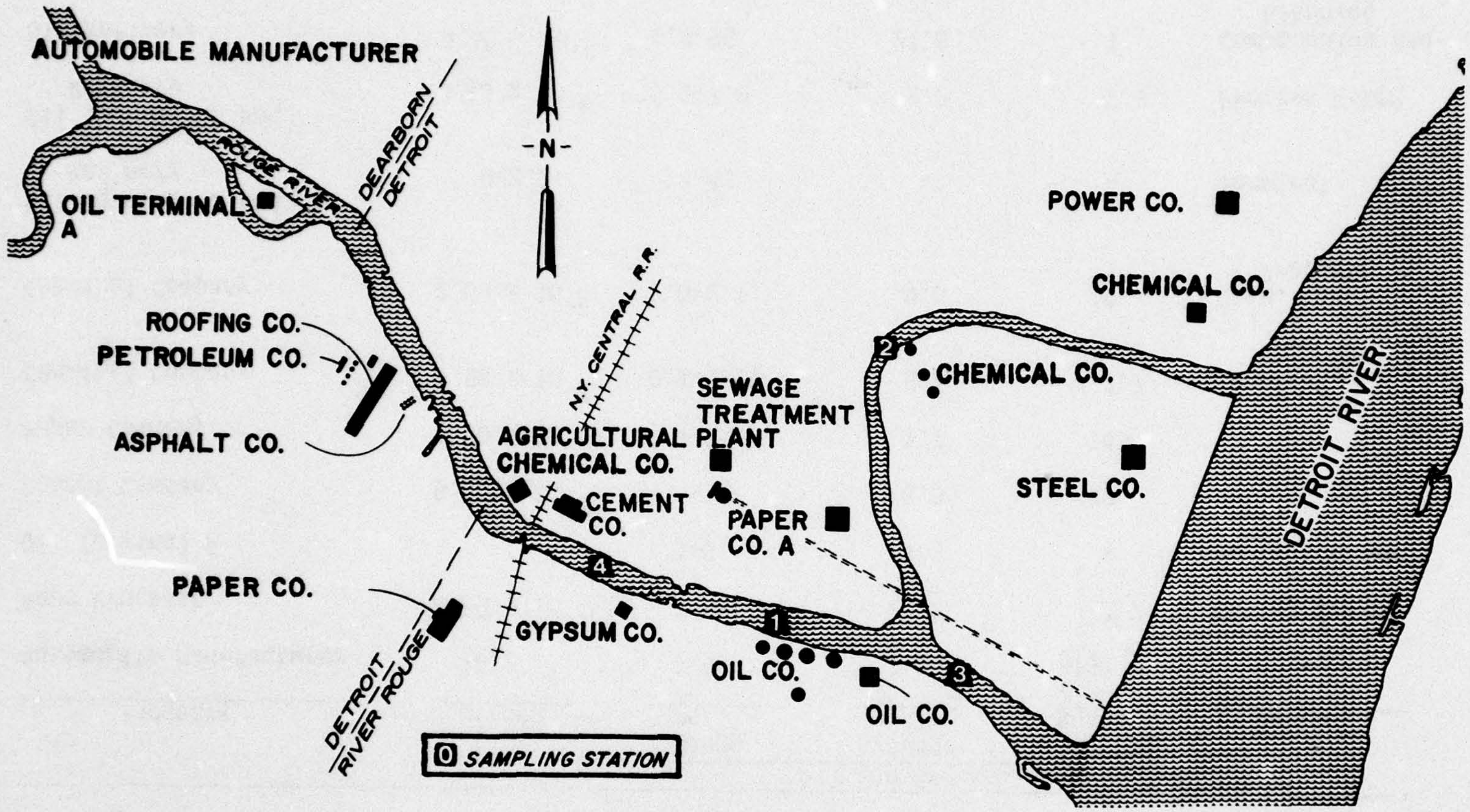

Figure 15. Sampling Locations - Rouge River

Table 9

NPDES Permitted Discharges
for Industries at Brunswick Harbor, Georgia

Industry	Flow m^3/sec	Oil and Grease Average mg/l	Oil and Grease Maximum mg/l	Source
Chemical Company	2.93×10^{-1}	*	*	Cooling Water
Power Plant				
Outfall 001	-	50	100	Boiler Blowdown
Outfall 002	-	50	100	Low Volume Waste
Outfall 003	-	15	20	Softened Blowdown
Pulp and Paper Mill	2.95	*	*	-
Waste Treatment Plant	1.28×10^{-1}	*	*	-

* No requirement specified.

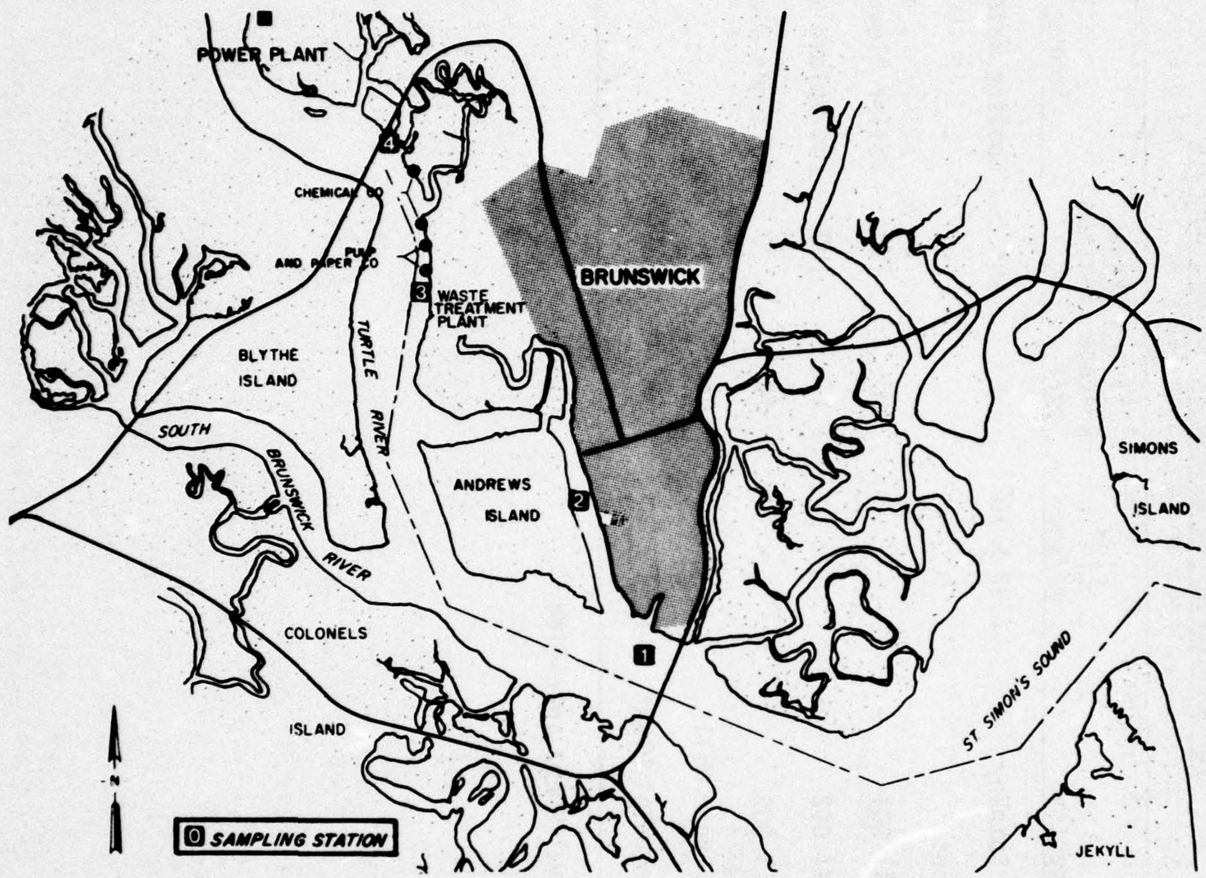

Figure 16. Sampling Locations - Brunswick Harbor

112. The power plant uses No. 5 bunker C oil to produce electricity. It discharges at three outfalls that flow to the Turtle River, Gibson Creek, and Cowpen Creek. The NPDES permit limitations issued by the EPA for these industries are shown in Table 9. Oil and grease levels in the discharges varied from 6 to 15 mg/l during a three-month monitoring period, well within the requirements of the NPDES permit.

Houston Ship Channel

113. The Houston Ship Channel is one of the most highly industrialized waterway segments in the Nation. Major industries in the vicinity of the Houston Ship Channel include petroleum refineries as well as chemical, steel, paper, and power plants.

114. Major industries along the channel as well as their discharge limitations on oil and grease are summarized in Table 10. Although the measurement of oil and grease levels is required in the NPDES monitoring report, the self-reporting data on oil and grease were not available for review. It is realized that the values in the NPDES permit may deviate from the actual plant discharges; however, these limitations are the upper limit for allowable discharges of oil and grease.

115. The location of the sampling stations and major oil and grease dischargers are shown in Figure 17. Sampling locations were selected to coincide with dredging schedules as well as to include significant oil dischargers. It is believed that these sampling points cover a good cross section of the channel and provide a broad data range for interpretation and analysis.

116. Several dredged material disposal sites are located along the channel. The dredged material is pumped directly from the channel bottom to the diked containment area by pipeline. The locations of these disposal sites are also shown in Figure 17.

117. The sampling stations in the Houston Ship Channel were located in two different parts of the channel. Stations 1 through 5 were in the upper part of Buffalo Bayou above the confluence with Greens Bayou. Stations 6 through 8 were in the lower section of the San Jacinto River near the entrance to Galveston Bay.

Table 10

Effluent Limitations

on Oil and Grease in Treated Industrial Effluents

Houston Ship Channel

Industry	Allowable Oil and Grease Effluent Average kg/day	Maximum kg/day
Regional Industrial Waste Treatment Plant	2,232	4,464
Oil Refinery A	972	1,831
Power Company	6.8	9.1
Chemical Company A	15*	30*
Oil Refinery B	-	75*
Steel Company A	62.7	170
Oil Refinery C	6.8	16
Paper Company A	-	-
Oil Refinery D		
Process Waste	20*	40*
Ballast Waste	8*	15*
Steel Company B	118	231
Chemical Company B	-	-
Oil Refinery E	-	15*
Chemical Company C	-	-
Oil Refinery F	62.2	108
Oil Refinery G	10-25*	12-30*

* Number expressed in mg/l; no flow requirements are specified.

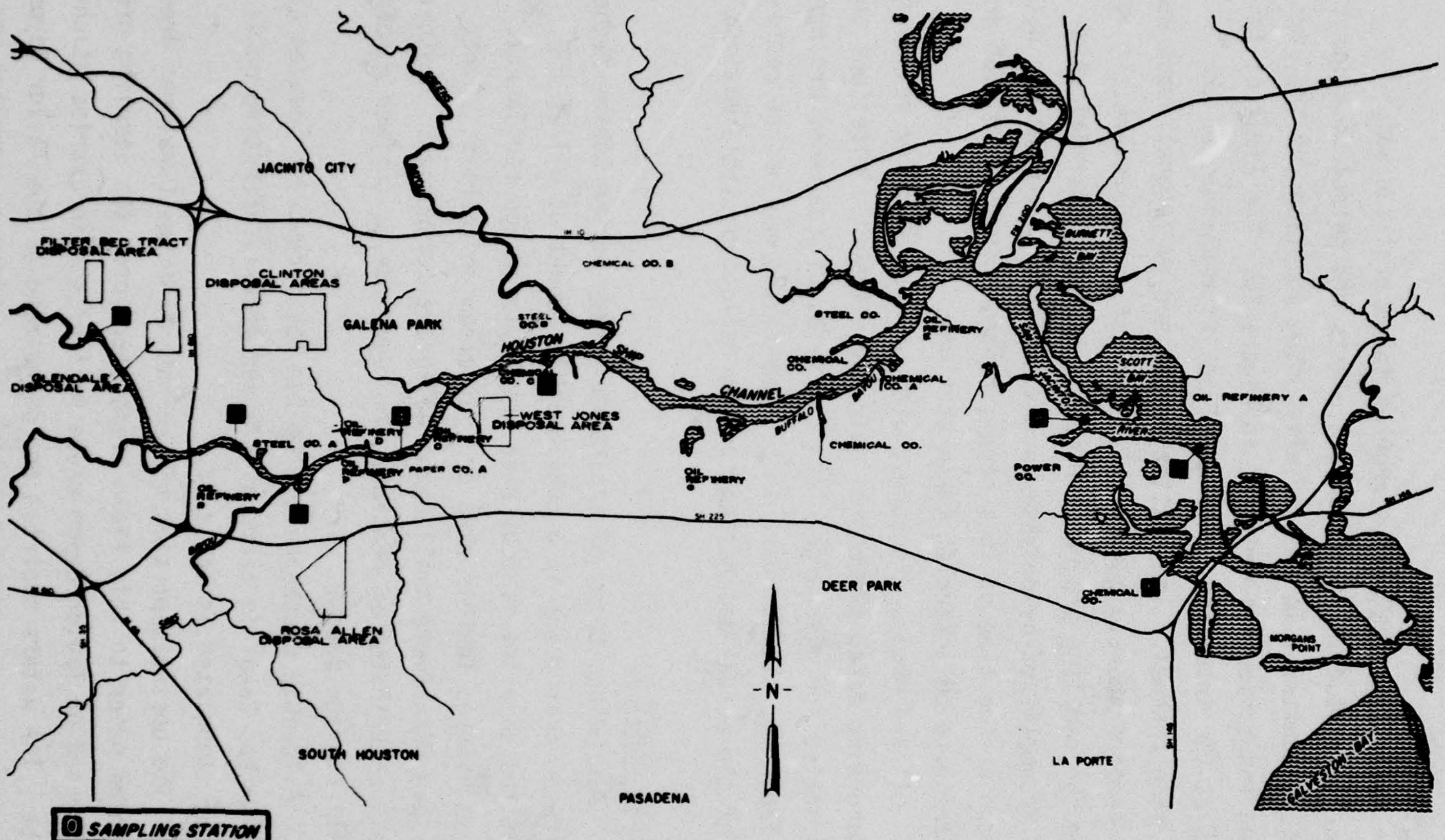

Figure 17. Sampling Locations - Houston Ship Channel

Texas City Channel

118. Texas City Channel is another industrialized waterway selected for this study. Petrochemical plants and petroleum refineries are the major industries in the vicinity. The locations of the sampling stations and industries are depicted in Figure 18. The limit of federal dredging is at the intersection of the Texas City Harbor and the industrial ship channel. The section maintained by federal funds was completely dredged shortly before this field study; therefore, it was not included in the sampling program. Dredging of the industrial ship channel is accomplished by private contractor. This segment was not being dredged at the time of this study; hence, only the sediment and water samples were collected at these stations.

119. Oil and grease discharges are not available for review from the self-reporting data; therefore, only the effluent limitations on oil and grease stated for discharges into the Texas City Channel are presented in Table 11. It is noted that these values may not be representative of the actual discharges, but do reflect possible maximum oil loads.

Sabine-Neches Canal

120. A previous Corps of Engineers survey at the Sabine-Neches Canal indicated that there is a considerable amount of oil in the sediment at the sampling station near the Taylor Bayou confluence.[39] The major industries in this area are petroleum refineries. Other industries are relatively small compared to the refineries. Another possible oil contributor of considerable magnitude is surface runoff from the oil storage areas.

121. Allowable discharge limits for the industries located along the Sabine-Neches Canal in terms of oil and grease, effective until June 30, 1975, are tabulated in Table 12.

122. The upstream portion of the Sabine-Neches Canal was dredged several months prior to this field trip; therefore, the sampling program was concentrated on Taylor Bayou where most of the industries discharge their waste. The waters upstream and downstream of the Taylor Bayou confluence were also surveyed for reference. Since no dredging was

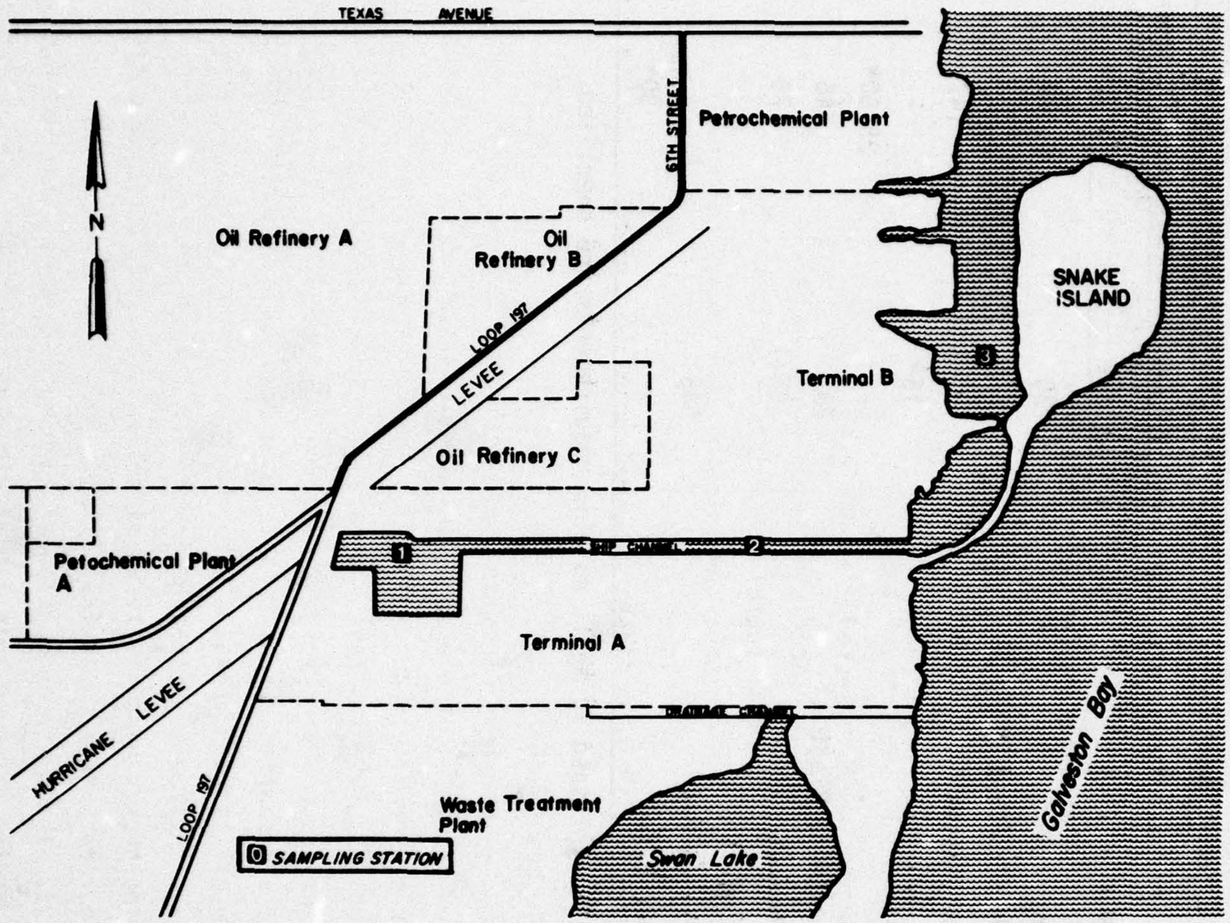

Figure 18. Sampling Locations - Texas City

Table 11

Effluent Limitations on Oil and Grease

Texas City Channel

Industry	Oil and Grease in Treated Effluent Monthly Average kg/day	Daily Maximum kg/day
Oil Refinery A	4,790	9,579
Petrochemical Plant A		
Process Wastes	81.3	147
Storm Runoff	15*	-
Terminal	-	25-50*
Waste Treatment Plant	297	446
Oil Refinery B	68.1	170
Oil Refinery C		
Process Wastes	545	-
Ballast Water	-	30*

* Numbers expressed in mg/l; no flow requirements are specified.

Table 12

Oil and Grease Effluent Limitations

Sabine-Neches Canal, Port Arthur, Texas

Industry	Oil and Grease in Treated Effluent Monthly Average kg/day	Daily Maximum kg/day
Oil Tank Farm A		
Outfall 001	79.5	159
Outfall 005	114	318
Outfall 006	7.7	19
Outfall 003	-	20*
Oil Refinery A		
Outfall 001	4,086	11,804
Outfalls 002-011	10-100*	15-205*
Oil Refinery B		
Outfall 001	5,652	11,304
Outfall 002	2,524	5,049
Outfall 003	284	568
Steel Company A	4.72	9.44

* Numbers expressed in mg/l; no flow requirements are specified.

underway at the time of this study, only water and sediment samples were collected for laboratory analysis. The locations of the sampling stations and the industries are shown in Figure 19.

Sampling Program

123. The field sampling program was designed to provide the data for (1) evaluation of the potential problem of oil release from dredged sediments and (2) investigation of the relationships between oil in solid and aqueous phases, such that a prediction of the oil level in return flows could be made. In this sampling program, oil levels in the sediments, water column, and return water were measured, as were other factors potentially affecting the release of oil from dredged sediments.

124. Sampling trips were planned, when possible, so as to coincide with dredging operations. Unfortunately, due to time constraints, it was not possible to schedule all of the trips at times when dredging was underway. No samples for either the sediment/water slurry or the containment area return flow could be taken at the Rouge River, Brunswick Harbor, Texas City Channel, or Sabine-Neches Canal sampling sites.

125. In order to provide an adequate data base for later analysis, it was decided that additional samples of return flow could be collected in the Houston area since maintenance dredging was underway. A three-week sampling program was conducted at three containment areas on the Houston Ship Channel during a period of dredging, and several samples of both the sediment/water slurry and containment area return flow were secured. Additional sampling was also conducted on the Sabine-Neches Canal by staff of the Corps of Engineers Galveston District Office.

126. At those sites where dredging was not being conducted at the time of sampling, water and sediment samples were collected from areas in which available data indicated a high oil content. The modified elutriate test, described in the following section, can be used to assess the potential for the release of oil during dredging operations at these locations. Though the modified elutriate test is not as

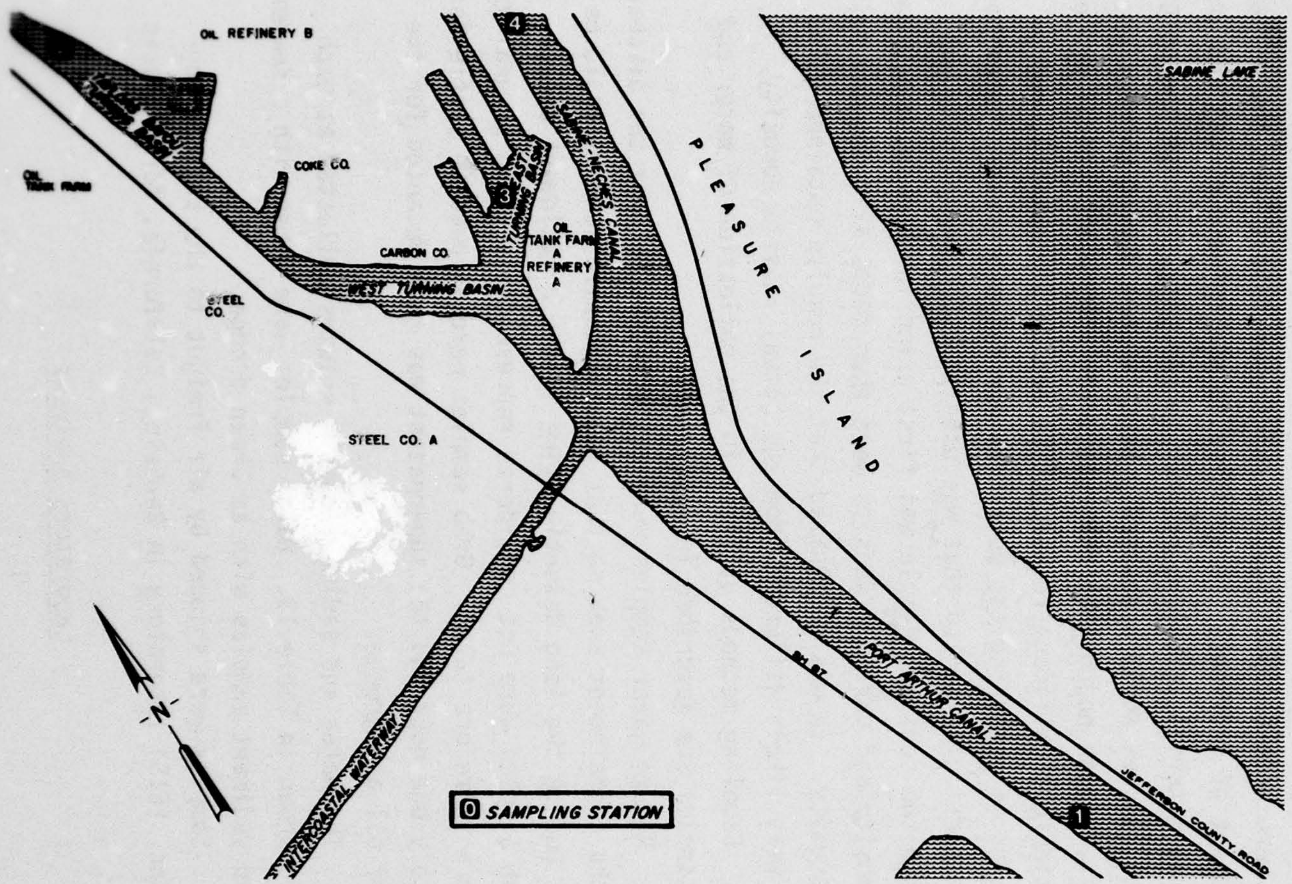

Figure 19. Sampling Locations - Sabine-Neches Canal

desirable as obtaining actual samples during dredging operations, the use of the test ensured that some sediments with high oil contents were sampled.

127. Estimates of the in situ sediment porosity were made. These estimates were made because it was considered possible that the oil and grease content of sediments, in addition to the release of oil and grease from dredged material, might be related to porosity. Though the porosity of sediment samples would undoubtedly be disturbed during extraction and transit, it was hoped that the relatively simple analytical procedure might elucidate significant relationships and be a practical, reproducible means of assessing the potential for oil and grease contamination. The particular method that was used to estimate porosity was one in which the sediment sample was first dried in an oven; measurements of bulk density and particle density were then made, allowing the calculation of porosity. It was recognized that the results obtained using this procedure were likely different from the actual in situ porosity.

128. Sampling methods utilized in the collection of water and sediment samples are described in Appendix A.

129. Return water samples were collected at or near the discharge point of the containment area so that representative samples could be obtained. Due to the long detention time in the containment areas, single grab samples were not considered representative, and several grab samples were therefore taken. Grab samples were allowed to settle for approximately one hour and the supernatant was then decanted for the analysis of oil and grease.

130. The water and sediment sample volumes collected at each station are shown in Table 13. Water samples were taken with a Kemmerer sampler and sediment samples with an Ekman dredge.

131. Samples were shipped by air freight to the Engineering-Science, Inc. (EIS) laboratory in Berkeley, California, for analysis.

Laboratory Analyses

132. Laboratory analyses conducted on water and sediment samples collected during the field sampling program are shown in Table 14.

Table 13

Sample Volume Collected

Station Type	Sample Type - Volume, l		
	Water Before Dredging	Water After Dredging	Sediment
Dredging Site	4	-	2
Containment Area Influent (Pump Discharge)	-	1.5*	-
Containment Area Effluent	-	1.5	-

* A 1.5-l sample of the pump discharge was collected at each dredging site.

Table 14

Types of Analyses

Analysis	Sample Type	Station Type: Dredging Site	Station Type: Containment Area Influent (Pump Discharge)	Station Type: Containment Area Effluent
Oil and Grease	Water	X	X	X
	Sediment	X	-	-
pH	Water	X	-	-
Temperature	Water	X	-	-
Conductivity	Water	X	-	-
Total Residue	Water	X	-	X
Dissolved Oxygen	Water	X	-	-
Porosity	Sediment	X	-	-
Particle Size	Sediment	X	-	-
Total Suspended Solids (TSS)	Water	X	X	X
Oil and Grease in Elutriate*	Sediment	X	-	-

* Triplicate analyses were performed.

These analyses were considered to be pertinent to the process of oil release from dredged material.

133. Most of the analyses listed in Table 14 are straightforward, with most analytical procedures taken directly from the 13th Edition of Standard Methods for the Examination of Water and Wastewater.[43] The laboratory procedures used during the course of this study are identified in Appendix A.

134. The freon extraction-gravimetric detection method was used on all samples for the oil and grease analysis. Samples showing relatively high oil and grease concentrations were analyzed for the content of petroleum (nonpolar) hydrocarbons.

135. A modified version of the standard elutriate test was used in the analysis of sediment samples. The standard elutriate test is designed to simulate the dredging process and thereby allow for the estimation of the amount of certain chemical constituents that would be released by dredging. These chemical constituents of the sediments may be dissolved in the interstitial water of the sediment or else migrate from the solid phase to the dissolved phase and thereby be released during dredging. In the standard elutriate test, the ratio of sediment to water (1:4) simulates the mixing that occurs during dredging. Due to the nature of oily materials, it was necessary for the purposes of this study to modify the standard elutriate test. The standard test calls for filtration of the elutriate through a membrane filter (0.45-μ pore size). Since removal of a substantial portion of the free and emulsified oil and grease would likely result from the filtration step, filtration was omitted from the elutriate test used in this study.

Results

136. The analytical results for the field samples collected at the six sampling sites are presented in tabular form. For each sampling site, an evaluation of the analytical results is presented separately. A discussion of the linear regression analyses performed on the results is presented following the evaluation of the analytical results.

137. As indicated in Part II, measurements of oil and grease at low concentrations show a high degree of variability. Also, the problem of obtaining representative samples is acute at low oil and grease concentrations. In light of these considerations and the small amount of data collected at each site, the results of the field sampling program, particularly the regression analyses, must be interpreted with care.

Evaluation of field study data -
Cuyahoga River, Cleveland

138. The analytical results for samples collected in the Cuyahoga River, Cleveland, are tabulated in Table 15. The oil and grease level in the sediment ranged from 2,030 to 5,170 mg/kg of dry sediment. With the exception of the sample collected at Station 4, most of the oils in the sediment were nonpolar in nature, indicating a petroleum origin. Water samples collected from the barge contents at Stations 1 and 2 showed an oil concentration of 1.0 and 1.8 mg/l, respectively. These oil and grease levels are slightly lower than the concentrations found in the elutriate solutions using sediments from the same stations. The highest oil and grease concentration in all of the elutriate tests was 6.4 mg/l.

139. Return water from the effluent weir at the containment area contained 0.4 mg/l oil with a total suspended solids (TSS) concentration of 169 mg/l. This oil concentration should not present any problem considering that the discharge limit set for Cleveland Port, Lake Erie, on oil and grease is 10 mg/l (see Table 1).

140. Water samples taken downstream of the dredge showed no adverse effects on water quality in terms of the oil and grease levels. The oil and grease concentrations measured at all stations in the Cuyahoga River were less than 1.5 mg/l.

Evaluation of field study data -
Rouge River, Detroit

141. A summary of the test data for samples collected at the Rouge River site are shown in Table 16. Sediment samples from Stations 2 and 4 showed relatively little oil. On the other hand, sediment samples from Stations 1 and 3 contained large quantities of oil.

Table 15

Summary of Test Data - Cuyahoga River, Cleveland

Parameter	Sample Identification				
	Station 1	Station 2	Station 3	Station 4	Return Water
WATER					
Oil and grease concentration, mg/l	0.4	0.4	1.0	1.4	0.4
TSS concentration, mg/l	29.2	27.6	48.4	28.4	169.0
Total residue concentration, mg/l	528.0	512.0	54.4	600.0	NM
Dissolved oxygen concentration, mg/l	1.2	1.2	3.3	1.0	NM
Conductivity, μmhos/cm	100*	100*	100*	100*	NM
SEDIMENT					
Oil and grease concentration, mg/kg	5,170	5,050	3,320	2,030	---
Percent solids	48.4	42.6	44.8	52.2	---
Percent nonpolar oil	76.0	75.0	92.0	7.8	---
Elutriate oil concentration, mg/l	3.0/4.5/4.0**	3.8/5.2/6.4**	3.8/5.0**	1.6/2.0/3.0**	---
Percent porosity	79.0	73.0	69.0	66.0	---
Particle size (μ):†					
50 percent smaller than	14	8	5	NM	---
80 percent smaller than	35	20	14	NM	---

* Approximate minimum sensitivity.

** Multiple samples.

† Micron (μ) = 10^{-6} m

Note: NM - Not Measured.

Table 16

Summary of Test Data - Rouge River, Detroit

Parameter	Sample Identification				
	Station 1	Station 2	Station 3	Station 4	Return Water
WATER					
Oil and grease concentration, mg/l	1.6	1.6	1.0	3.6	1.6
TSS concentration, mg/l	54.0	35.2	29.2	34.0	43.2
Total residue concentration, mg/l	516	400	364	1,150	266
Dissolved oxygen concentration, mg/l	6.0	6.8	5.8	5.8	NM
Conductivity, μmhos/cm	100*	100*	100*	100*	NM
SEDIMENT					
Oil and grease concentration, mg/kg	32,200	386	7,260	1,728	---
Percent solids	42.6	79.5	57.0	78.3	---
Percent nonpolar oil	85	100	78	86	---
Elutriate oil concentration, mg/l	2.8/3.0/3.2**	0.1/0.5/0.7**	4.6/5.2**	1.2/1.4/1.4**	---
Percent porosity	73.0	47.0	70.0	49.0	---
Particle size (μ):†					
50 percent smaller than	10	20	38	70	---
80 percent smaller than	30	70	85	NM	---

* Approximate minimum sensitivity.

** Multiple samples.

† Micron (μ) = 10^{-6} m

Note: NM - Not Measured.

The proximity of Station 1 to an oil tank farm may explain the high level of oil in the sediment, as there may have been an oil spill or long-term contributions of oil by surface runoff. Essentially all of the oil in the sediments was of petroleum origin.

142. The range of oil concentrations measured in the elutriate tests on the sediment and water samples was from 0.1 to 5.2 mg/l. Although the elutriate from the sediment sample at Station 1 had very little oil, the oil content in the sediment exceeded three percent by weight. The results of a sieve analysis showed that the particle size distribution of the sediment sample is much smaller at Station 1 than at the other stations. This smaller particle size may be a factor in the high oil concentrations in the sediment, as the greater surface area associated with smaller particle sizes affords more oil adsorbent area.

143. One return water sample was collected at the Grassy Island disposal site. The oil content in the sample collected from the effluent weir was 1.6 mg/l. This oil concentration is approximately equal to levels found in water samples collected at the four river sampling stations.

Evaluation of field study data -
Brunswick Harbor, Georgia

144. Analytical results on samples from Brunswick Harbor, Georgia, are summarized in Table 17. The oil and grease levels in the sediment samples taken at these stations were low. Most of the channel was dredged prior to this field sampling trip, and it is reasonable to assume that the actual oil levels are as low as the analytical results show. The portion of the waterway at Station 2 was not included in the dredging project. Although it had not been dredged recently, the oil and grease levels at Station 2 were consistent with those at the other three stations. However, a study conducted in July 1975 by the Corps of Engineers showed an oil level as high as 10 percent by weight at Station 2.[42] Errors inherent in grab sampling may account for this discrepancy, as well as the much smaller size of particles at Station 2.

145. Elutriate oil and grease concentrations ranged from 0.2 to 1.4 mg/l. It is noted that a relatively low fraction of the oil and

Table 17

Summary of Test Data - Brunswick Harbor

Parameter	Sample Identification Station 1	Station 2	Station 3	Station 4
WATER				
Oil and grease concentration, mg/l	1.2	0.4	0.8	0.4
TSS concentration, mg/l	322	216	240	228
Total residue concentration, mg/l	25,414	25,484	24,304	23,600
pH	7.3	7.6	7.6	7.6
Dissolved oxygen concentration, mg/l	4.7	4.8	4.4	3.7
Conductivity, μmhos/cm	42,000	23,000	42,000	35,000
SEDIMENT				
Oil and grease concentration, mg/kg	216	178	213	238
Percent solids	44.5	19.0	54.9	44.3
Percent nonpolar oil	5.6	17.0	38.0	40.0
Elutriate oil concentration, mg/l	1.2/1.4*	0.2/0.3/0.4*	0.3/0.3/0.6*	0.7/0.7/1.4*
Percent porosity	76.0	84.0	62.0	70.0
Particle size (μ)**				
50 percent smaller than	60	1.3	70	50
80 percent smaller than	NM	2.0	NM	NM

* Multiple samples.

** Micron (μ) = 10^{-6} m

Note: NM - Not Measured.

grease was nonpolar hydrocarbons, which indicates most of these oils are not of petroleum origin.

Evaluation of field study data - Houston Ship Channel

146. A summary of the data is presented in Table 18. Oil and grease concentrations in the sediment samples collected at the Houston Ship Channel ranged from 307 to 6,700 mg/kg. The oil content in the sediment decreased as the sampling stations approached Galveston Bay. There is more influence by tributary flow, tidal action, and wind in the lower reaches of the channel, resulting in higher average velocities in the cross section. A small, oil-coated particle that might be deposited in the upper reach of the channel could be carried by the flow and tidal and wind action into Galveston Bay. This speculation is supported by the results of the particle-size analyses, which showed large particle sizes in the sediment samples from Stations 6, 7, and 8, indicating that the smaller, lighter particles have been washed out into Galveston Bay. In addition, most of the major point-source discharges are in the upstream segment of the channel.

147. Results of elutriate tests using these sediment samples range from 0.1 to 1.4 mg/l. This concentration range was lower than the oil and grease concentrations found in the water used for the elutriate tests, indicating that the sediments adsorbed oil from the water rather than releasing it to the water. It is also possible, however, that oil plated out on the container and was not detected by the analysis or that the oil was associated with suspended solids removed by centrifugation in the elutriate tests.

148. Three dredged material disposal sites along the Houston Ship Channel were monitored for a period of three weeks. The effluent return water at the spillway was collected and analyzed for oil and grease and TSS. The results of these analyses are shown in Table 19. Oil and grease contents in the return waters ranged from trace amounts to 13.3 mg/l. In general, the return flow oil and grease concentrations were quite low (1.0 to 2.0 mg/l) with occasional peaks that tended to raise the mean concentration substantially. The cause of these peaks is

Table 18

Summary of Test Data - Houston Ship Channel

Parameter	Sample Identification							
	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7	Station 8
WATER								
Oil and grease concentration, mg/l	3.2	4.0	3.2	6.6	6.2	3.3	3.2	3.0
TSS concentration, mg/l	70.8	87.2	98.0	100.0	98.0	117.0	110.0	113.0
Total residue concentration, mg/l	9,400	10,000	10,900	10,200	11,900	17,800	17,300	16,500
pH	7.3	7.2	7.4	7.4	7.8	7.6	7.5	7.6
Dissolved oxygen concentration, mg/l	0.8	0.6	1.4	1.3	3.1	7.5	NM	NM
SEDIMENT								
Oil and grease concentration, mg/kg	1,740	5,660	6,700	3,430	634	307	541	644
Percent solids	33.7	36.9	28.6	27.9	30.9	53.1	37.9	57.6
Percent nonpolar oil	80	90	81	84	75	40	92	86
Elutriate oil concentration, mg/l	0.4/0.4/0.4*	1.0/1.2*	0.8/0.9/1.0*	1.0/1.2/1.4*	1.2/1.2/1.3*	0.7/0.7/0.8*	0.1/0.4/0.4*	0.1/0.1*
Percent porosity	88.3	78.7	83.0	89.9	87.7	71.7	93.5	58.4
Particle Size (μ):**								
50 percent smaller than	3.0	7.0	2.0	1.7	1.3	70.0	15.0	100.0
80 percent smaller than	40.0	36.0	9.0	6.5	3.0	NM	NM	NM

* Multiple samples.

** Micron (μ) = 10^{-6} m

Note: NM - Not Measured.

Table 19

Oil and Grease in Return Flows - Houston Ship Channel

Date	Clinton Site			Glendale Site			Jones Site		
	Oil & Grease mg/l	TSS mg/l	Percent Non-polar Oil	Oil & Grease mg/l	TSS mg/l	Percent Non-polar Oil	Oil & Grease mg/l	TSS mg/l	Percent Non-polar Oil
12/03/75	2.4	104	54.0	2.6	-	33.3	-	-	-
12/04/75	1.7	-	8.3	2.4	-	12.0	-	-	-
12/05/75	1.4	-	90.9	1.1	-	14.3	-	-	-
12/06/75	3.8	-	33.3	1.7	-	8.3	-	-	-
12/07/75	1.6	-	36.4	1.6	-	43.0	-	-	-
12/08/75	2.4	-	28.6	1.7	-	72.7	-	-	-
12/09/75	5.1	22.5	83.3	1.8	-	-	1.5	157	-
12/10/75	3.6	300	-	5.1	363	-	0.2	195	-
12/11/75	5.9	278	-	13.3	529	-	1.0	200	-
12/12/75	4.9	225	-	7.8	365	-	1.5	365	-
12/13/75	2.1	248	-	6.8	361	-	1.8	324	-
12/14/75	0.8	-	-	6.4	-	-	1.2	-	-
12/15/75	1.5	-	-	2.1	-	-	2.3	-	-
12/16/75	1.7	-	-	4.1	-	-	8.7	-	-
12/17/75	0.9	-	-	2.2	-	-	1.0	-	-
12/18/75	0.6	-	-	1.0	-	-	-	-	-
12/19/75	0.4	170	-	1.2	277	33.3	0.6	108	-
12/20/75	1.4	201	71.4	0.6	294	-	0.2	101	-
12/22/75	0.4	130	-	1.0	262	80.0	0.2	120	-
12/23/75	0.7	115	-	1.0	286	-	0.3	110	-
12/24/75	-	-	-	-	-	-	1.1	-	33.3
12/26/75	-	-	-	-	-	-	0.8	-	44.4
12/29/75	-	-	-	-	-	-	2.2	-	86.2
12/30/75	-	-	-	-	-	-	1.1	-	36.2
Average	2.2			3.3			1.5		

unclear as none of the supplementary environmental data indicate any unusual conditions. Kerosene is occasionally used for odor control at these sites but would not be expected to increase the measurement of oil in the return water since it is volatilized in the analytical procedure. Another possibility is that the oil measured is associated with suspended solids rather than being free oil. This possibility will be addressed in depth in a later section of this report.

149. Probability distributions of oil and grease levels from each disposal site are shown in Figures 20 through 22. Oil and grease levels from these disposal sites were less than 5.0 mg/l more than 75 percent of the time. A maximum value of 13.3 mg/l was measured during the sampling period.

150. In order to compare the results of the elutriate test and actual oil release from hydraulic dredging, pump discharges from the dredge were collected at different time periods during dredging operations at the Houston Ship Channel. Samples were analyzed for oil and grease in the sediment and in the supernatant. The oil and grease concentrations found in the settled sediment are assumed to be equivalent to in situ sediment samples because of the fact that only a very small fraction of oil is released from the sediment based on the elutriate test and return flow data. The analytical results are tabulated in Table 20.

151. When these data for oil and grease levels in the supernatant are compared to previously discussed elutriate tests results from the Houston Ship Channel site, the concentrations in these water samples are slightly higher than those found in the elutriates. This could be due to a higher level of TSS in the supernatant than in the centrifuged elutriate samples. Oil and grease levels in the elutriates averaged 0.97 mg/l in the Houston Ship Channel samples and the corresponding supernatant samples averaged 2.1 mg/l.

Evaluation of field study data -
Texas City Channel

152. The results of laboratory analyses on samples from Texas City Channel are tabulated in Table 21. As can be seen from the table,

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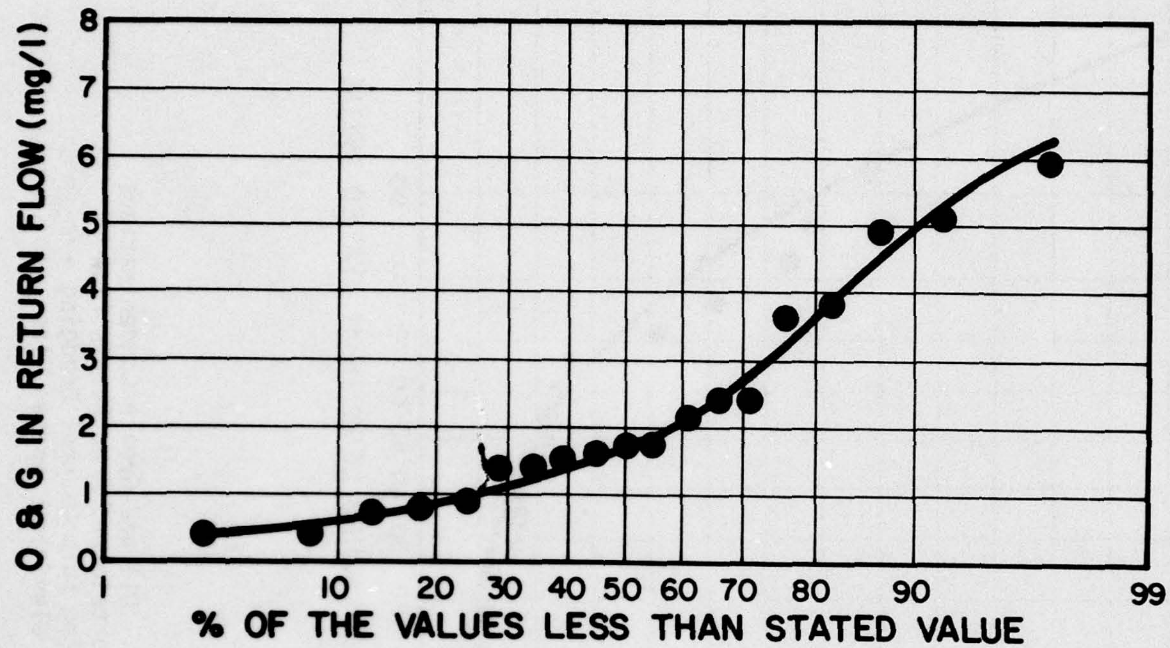

Figure 20. Oil and Grease Concentrations in Containment Area Return Flow
Houston Ship Channel Dredging - Clinton Disposal Site

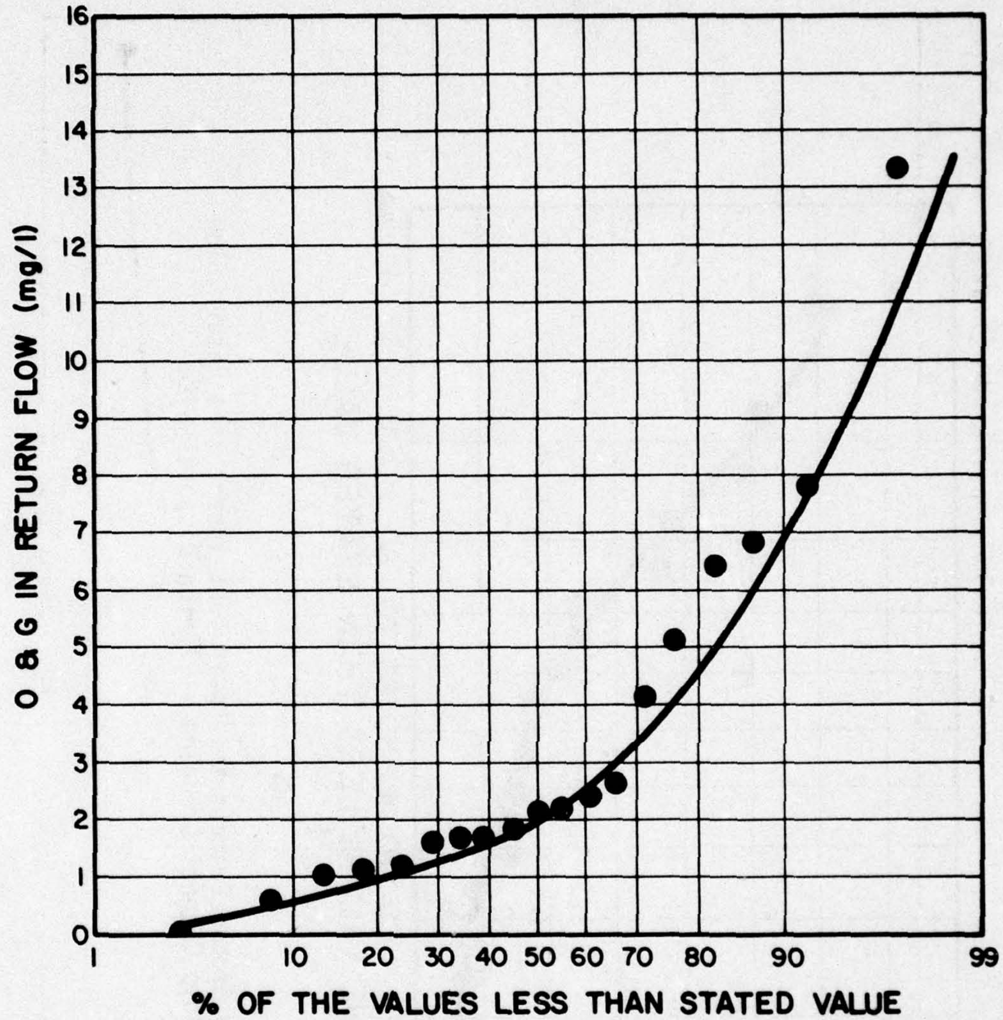

Figure 21. Oil and Grease Concentrations
in Containment Area Return Flow
Houston Ship Channel Dredging -
Glendale Disposal Site

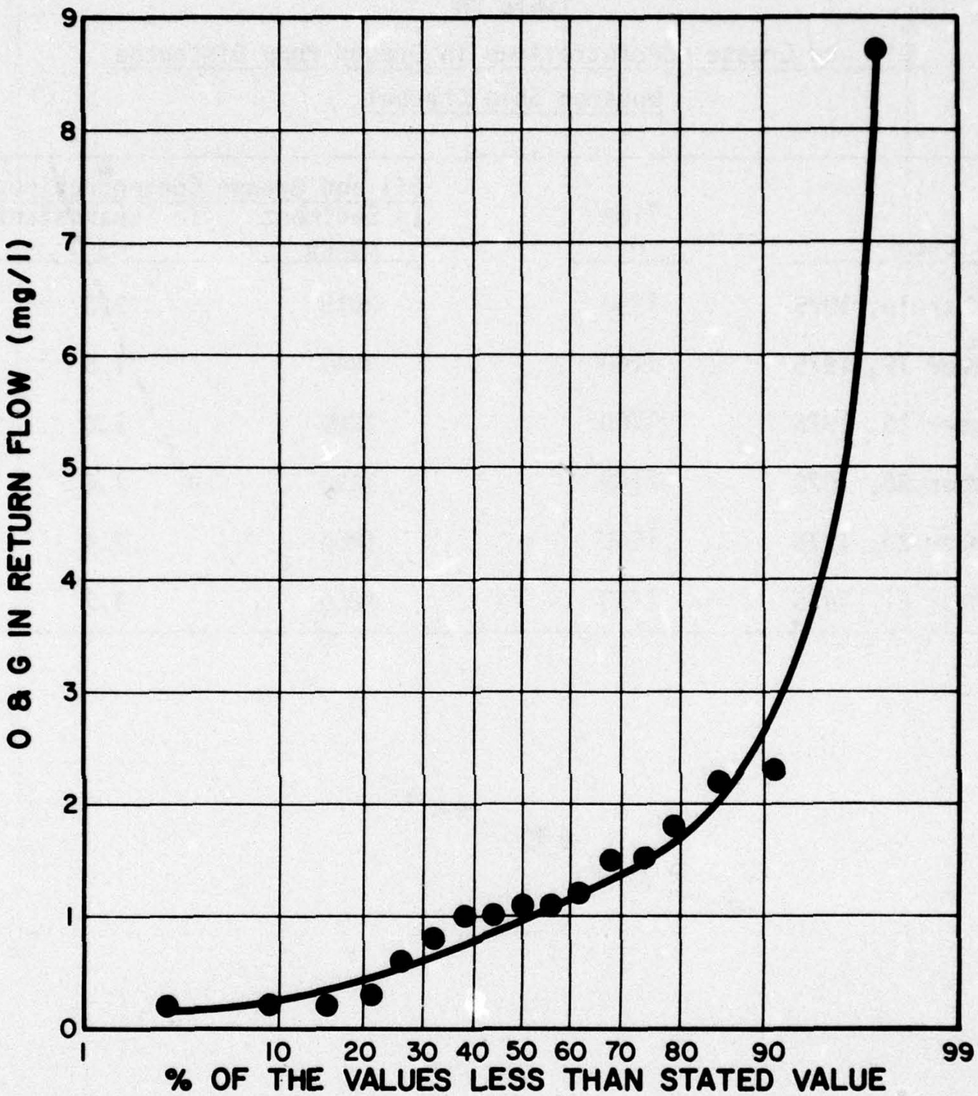

Figure 22. Oil and Grease Concentrations in Containment Area Return Flow Houston Ship Channel Dredging - Jones Disposal Site

Table 20

Oil and Grease Concentrations in Dredge Pump Discharge

Houston Ship Channel

Date	Time hr	Oil and Grease Concentrations In Sediment mg/kg	Oil and Grease Concentrations In Supernatant mg/l
December 18, 1975	1700	2010	3.3
December 19, 1975	1100	1840	1.5
December 19, 1975	1700	1680	2.0
December 20, 1975	2100	1290	1.6
December 20, 1975	1545	1860	2.4
December 21, 1975	1730	1820	1.7

Table 21

Summary of Test Data - Texas City Channel

Parameter	Sample Identification: Station 1	Station 2	Station 3
WATER			
Oil and grease concentration, mg/l	3.2	3.2	3.0
Nonpolar fraction of oil and grease concentration, percent	28	13	33
TSS concentration, mg/l	159	198	183
Total residue concentration, mg/l	28,700	28,700	28,500
pH	8.1	8.1	8.2
Dissolved oxygen concentration, mg/l	7.1	8.2	11.0
Conductivity, μmhos/cm	21,000	27,000	28,000
SEDIMENT			
Oil and grease concentration, mg/kg	557	1,606	651
Percent solids	49.0	32.3	51.7
Percent nonpolar oil	100	50	51
Elutriate oil concentration, mg/l	0.1/0.1*	0.8/2.3/2.4*	0.4/0.6/0.6*
Nonpolar fraction of elutriate oil concentration, percent	<2	<2	<2
Percent porosity	78.1	87.0	75.3
Particle size (μ)**			
50 percent smaller than	10	12	45
80 percent smaller than	22	50	NM

* Multiple samples.

** Micron (μ) = 10^{-6} metres.

Note: NM - Not Measured.

oil levels in the water and sediment phases were relatively low in comparison with other study sites. It is noted that a very low fraction of the elutriate oil is nonpolar and that a relatively low nonpolar fraction of oil and grease exists in the overlying water.

153. The point-source limitations on oil and grease discharges to Galveston Bay are typically 20 mg/l.

154. The Texas City Channel was dredged during the period from September to December 1974, and at that time a survey was conducted by the Corps of Engineers Galveston District Office to study the environmental impact on water quality by maintenance dredging.[40] This survey detected oil and grease levels in excess of 20 mg/l in certain parts of the channel. Moreover, the disposal areas along this channel are open (i.e., at the north end of the Texas City dike) or only partially confined (i.e., at Snake Island), which, along with the high levels of oil found during the Corps of Engineers' investigations, indicates that oil-laden sediments are being discharged back into the channel after dredging. The results of the monitoring study conducted by the Corps of Engineers Galveston District Office are plotted on a probability basis in Figure 23. As shown by the plot, about 25 percent of the time, oil and grease levels greater than 20 mg/l occur in the channel after dredging. It is unclear from these data, however, whether the measured concentrations represent free oils or oily substances bound to suspended sediment particles.

Evaluation of field study data - Sabine-Neches Canal

155. Table 22 lists the laboratory data for samples collected at the Sabine-Neches Canal in Port Arthur, Texas. Oil contents as high as three percent by weight were found for sediments sampled at Station 2. Small particle sizes with a corresponding high porosity were found in the sediment at all stations. The results of the elutriate tests showed no oil and grease concentration greater than 2.0 mg/l in the elutriate solution. Low percentages of nonpolar oil and grease were detected in the elutriate, indicating that petroleum hydrocarbons are less likely to be released by the elutriate technique.

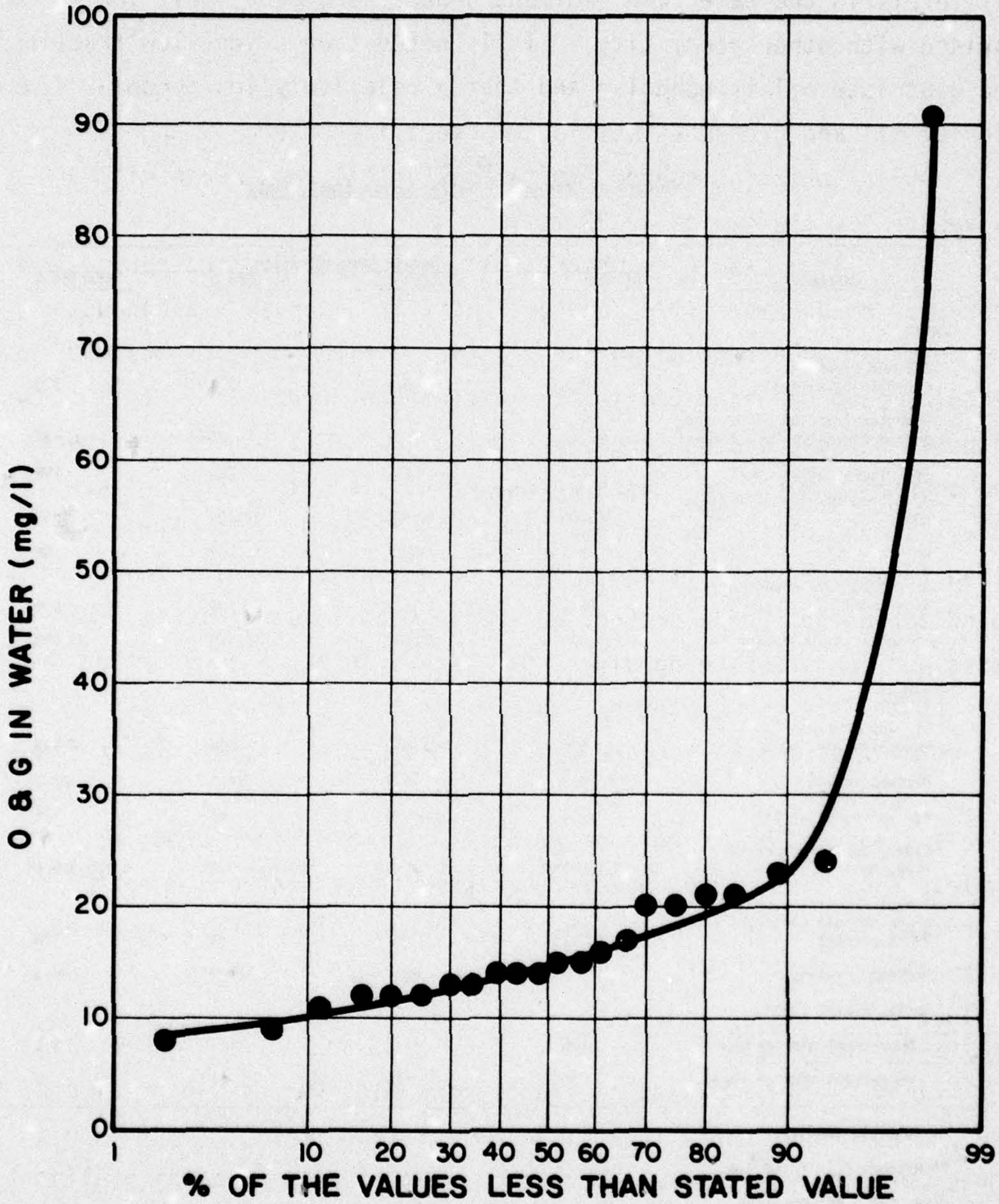

Figure 23. Oil and Grease Concentrations
in Containment Area Return Flow
Texas City Channel

Table 22

Summary of Test Data - Sabine-Neches Canal, Texas

Parameter	Sample Identification Station 1	Station 2	Station 3	Station 4
WATER				
Oil and grease concentration, mg/l	1.2	0.6	2.4	3.0
Nonpolar fraction of oil and grease concentration, percent	42	17	17	33
TSS concentration, mg/l	137	101	152	169
Total residue concentration, mg/l	18,200	12,900	22,600	22,100
pH	8.1	8.1	8.2	NM
Dissolved oxygen concentration, mg/l	6.5	5.7	6.6	6.9
Conductivity, μmhos/cm	31,000	27,000	31,000	32,000
SEDIMENT				
Oil and grease Concentration, mg/kg	576	31,000	893	733
Percent solids	28.9	19.9	24.3	27.2
Percent nonpolar oil	50	76	57	74
Elutriate oil concentration, mg/l	0.1/0.1/0.1*	1.2/2.0*	0.1/0.2/0.2*	0.1/0.3/0.4*
Nonpolar fraction of elutriate oil concentration, percent	<2	<2	<2	28
Percent porosity	85.3	88.4	88.9	87.3
Particle size (μ)**				
50 percent smaller than	1.5	1.5	1.5	1.5
80 percent smaller than	18	10	4	8

* Multiple samples.

** Microns (μ) = 10^{-6} m

Note: NM - Not Measured

156. The channel was not being dredged at the time of the initial sampling trip; therefore, no return water samples were available. However, data collected before maintenance dredging for a previous study by the Corps of Engineers were reviewed for comparison.[39] The results from that study indicated that the return water at the spillways from three disposal containment areas contained very little oil. Oil concentrations in samples collected during dredging ranged from trace amounts to 2.2 mg/l.

157. Return flow samples from a dredged material containment area on the Sabine-Neches Canal were collected by the Corps of Engineers staff and provided for analysis. These data are presented in Table 23. The highest recorded oil and grease level in the return water was only 1.6 mg/l.

Data Correlation

158. Field study data were statistically analyzed to determine the existence of any relationships between the various parameters measured. A number of linear regression analyses were performed and the results of these analyses, in terms of their correlation coefficients, are presented in Table 24. Examples of the correlation analyses are presented in Figures 24 through 28.

159. The significance of the data in Table 24 is two-fold: (1) for the available data, it is readily noted that no single set of regression analyses even displays the same sign of the correlation coefficient; that is, the directionality of the results is not consistent in any relationship; and (2) the magnitude of the correlation coefficients is often quite low.

160. The data, though not showing any clear-cut relationships, must be carefully interpreted for several reasons. As discussed in Part II, there is a significant degree of analytical variability associated with oil and grease measurements at low concentrations (as well as for sediment analyses even at high concentrations) and this could mask any relationship that may exist. The data base for a given location was

Table 23

Sabine-Neches Canal Maintenance Dredging

Main Channel

Sampling Date	Oil and Grease: Containment Area Return Flow mg/l	Oil and Grease: Dredge Discharge Supernatant mg/l	Oil and Grease: Sediment mg/kg	Sediment Percent Solids
4/15/76	0.3	2.2	417	29.3
4/16/76	0.6	1.1	354	38.1
4/19/76	0.1	0.5	628	23.6
4/20/76	1.3	1.3	343	26.4
4/21/76	0.7	1.7	510	36.3
4/22/76	0.9	3.0	387	39.9
4/26/76	0.9	1.3	181	30.0
4/27/76	1.0	2.3	424	27.4
4/28/76	0.8	1.9	360	28.3
4/29/76	1.4	-	-	-
5/03/76	1.6	-	458	29.8
5/04/76	0.6	1.7	349	35.2
5/05/76	0.8	1.3	397	21.4
5/06/76	0.3	1.4	428	39.6
5/07/76	0.6	-	365	44.0
5/11/76	0.6	2.9	544	23.4
Standard Deviation	0.4	0.7	-	-
Mean	0.8	1.7	-	-

Table 24

Linear Regression Correlation Coefficients

Correlation of Abscissa and Ordinate Parameters	Cuyahoga River	Rouge River	Brunswick Harbor	Houston Ship Channel Sample Locations 1-5	Houston Ship Channel Sample Locations 6-8	Texas City Channel	Sabine-Neches Canal
x = Porosity, percent y = Oil & Grease in Sediment, mg/kg	0.91	0.78[1]	-0.65	-0.73	-0.14	0.95	0.39
x = 50th Percentile Particle Size, μ y = Oil & Grease in Sediment, mg/kg	0.79	-0.60[2]	0.75[3]	0.44	0.13	-0.38	-
x = 80th Percentile Particle Size, μ y = Oil & Grease in Sediment, mg/kg	0.76	-0.88	-	0.08	-	-	-0.01[4]
x = Total Suspended Solids, mg/l y = Oil & Grease in Water, mg/l	0.27	-0.08	0.94	0.62	0.40	-0.61	0.95
x = Oil & Grease in Water, mg/l y = Oil & Grease in Elutriate, mg/l	-0.75	-0.54	0.60	0.75	0.92	-0.24	-0.67

NOTE: $\mu = 10^{-6}m$

[1] If the data point from Station 1 is excluded (since the station is located near an oil tank farm and surface runoff and/or oil spills may bias the actual relationship), the correlation coefficient is 0.99.

[2] If the data point from Station 2 is excluded (since the station is located on a branch of the main River, and the sediment oil content may not be related to sediment particle size by the same relationship, which appears to hold for the mainstream of the River), the correlation coefficient is -0.92.

[3] If the data point for Station 2 is excluded (the site was not dredged prior to the sampling effort whereas the others were), the correlation coefficient is -0.92.

[4] If the data point for Station 2 is excluded (due to the atypical water velocity at that point, the measurements are not characteristic of the rest of the Canal), the correlation coefficient is -0.97.

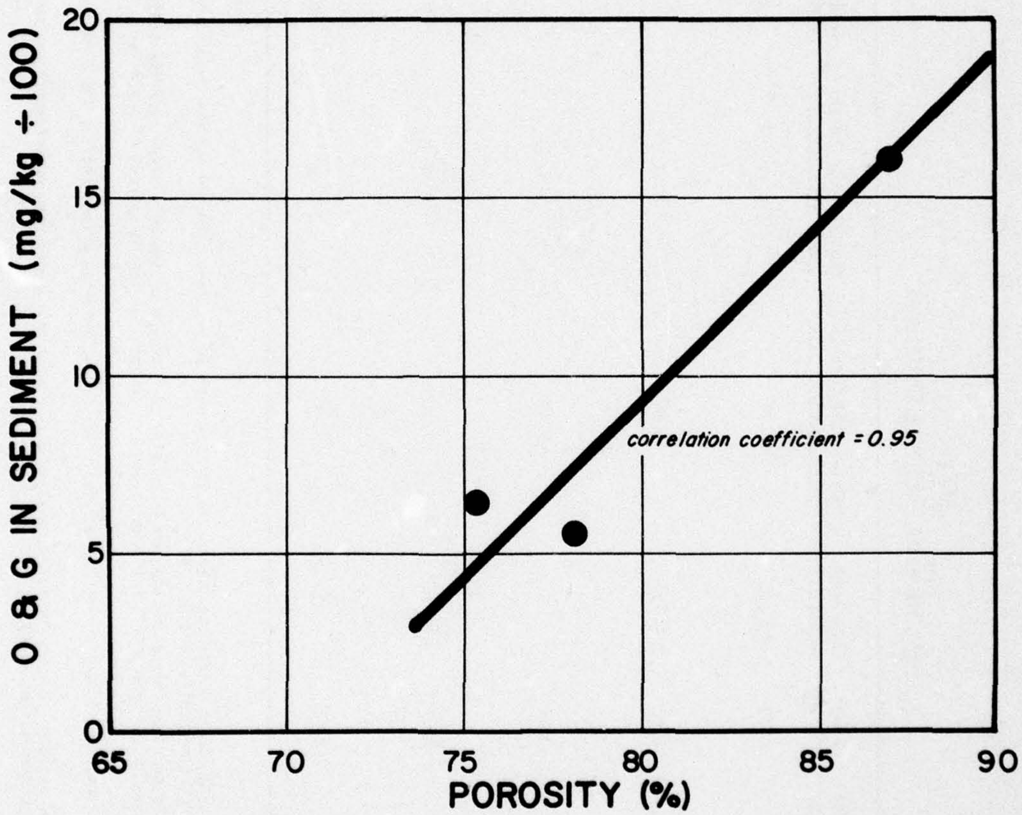

Figure 24. Data Correlations - Texas City Channel

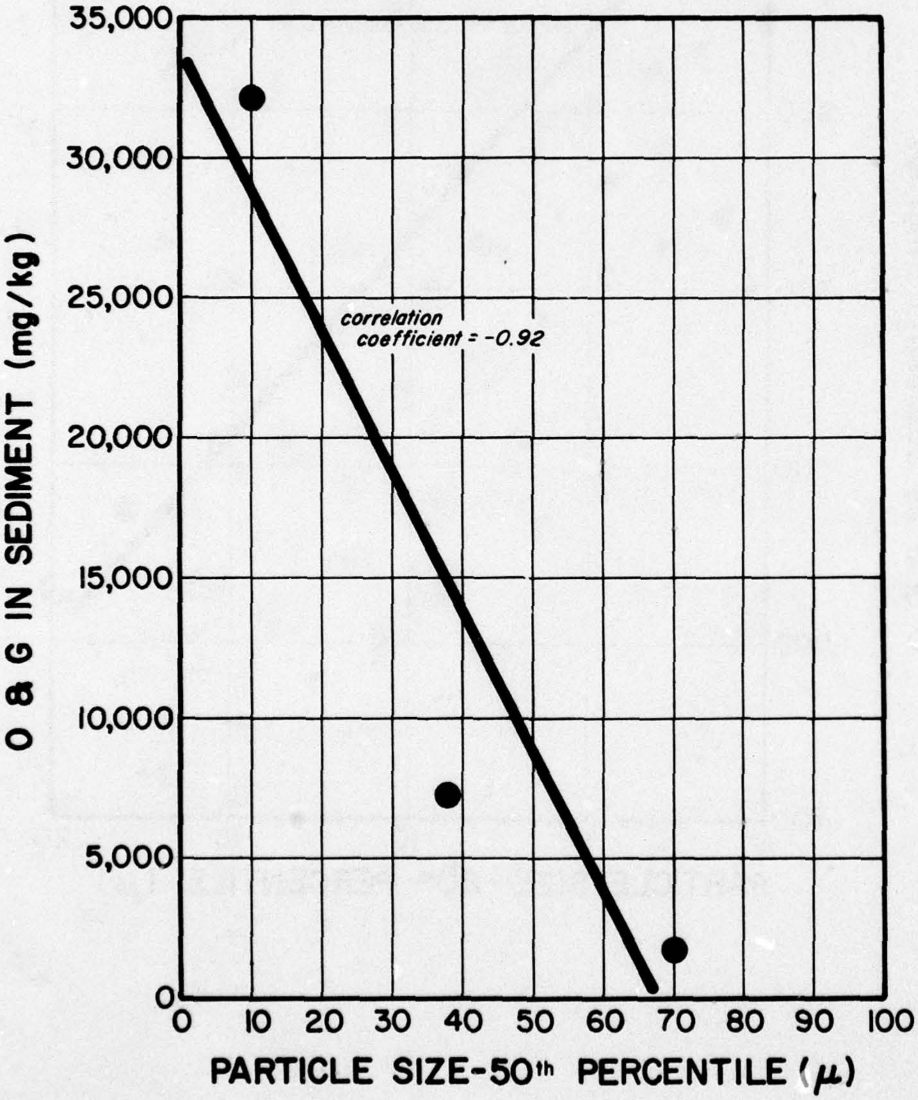

Figure 25. Data Correlations - Rouge River

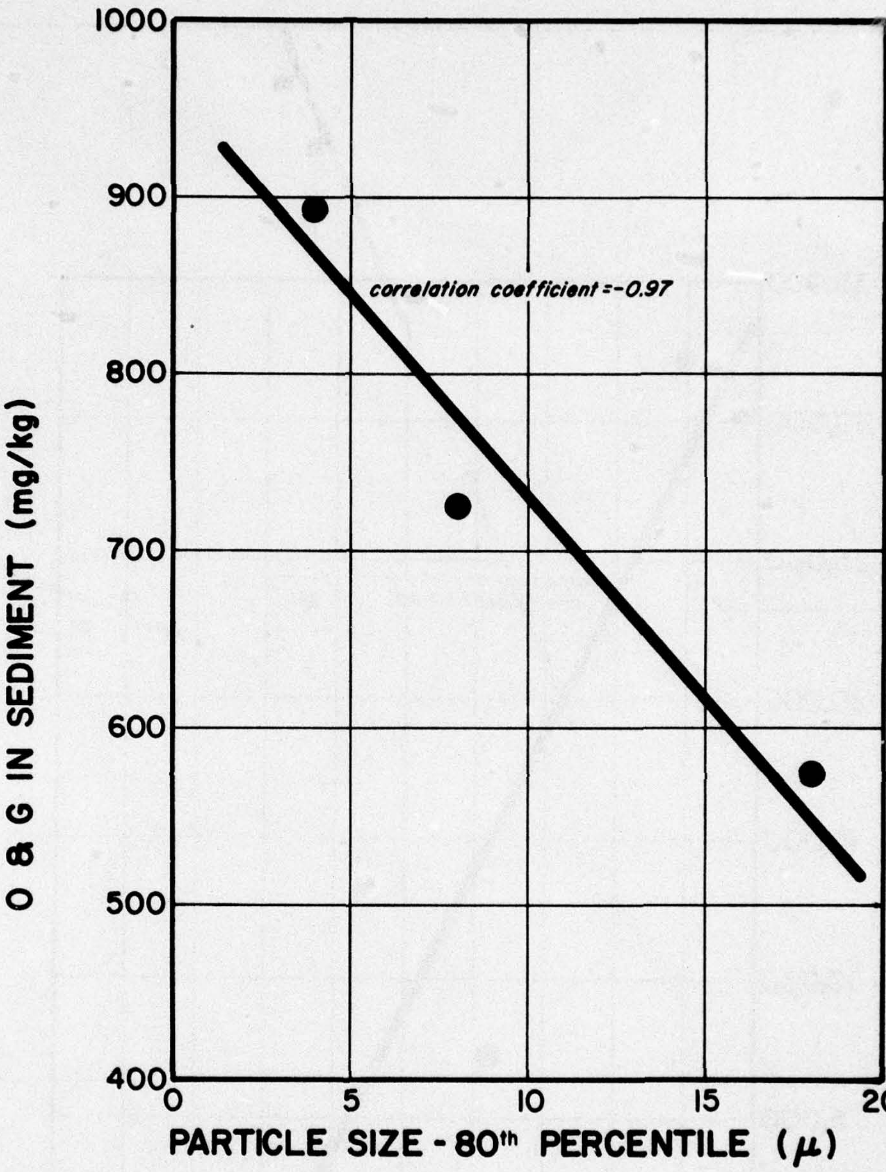

Figure 26. Data Correlations - Sabine-Neches Canal

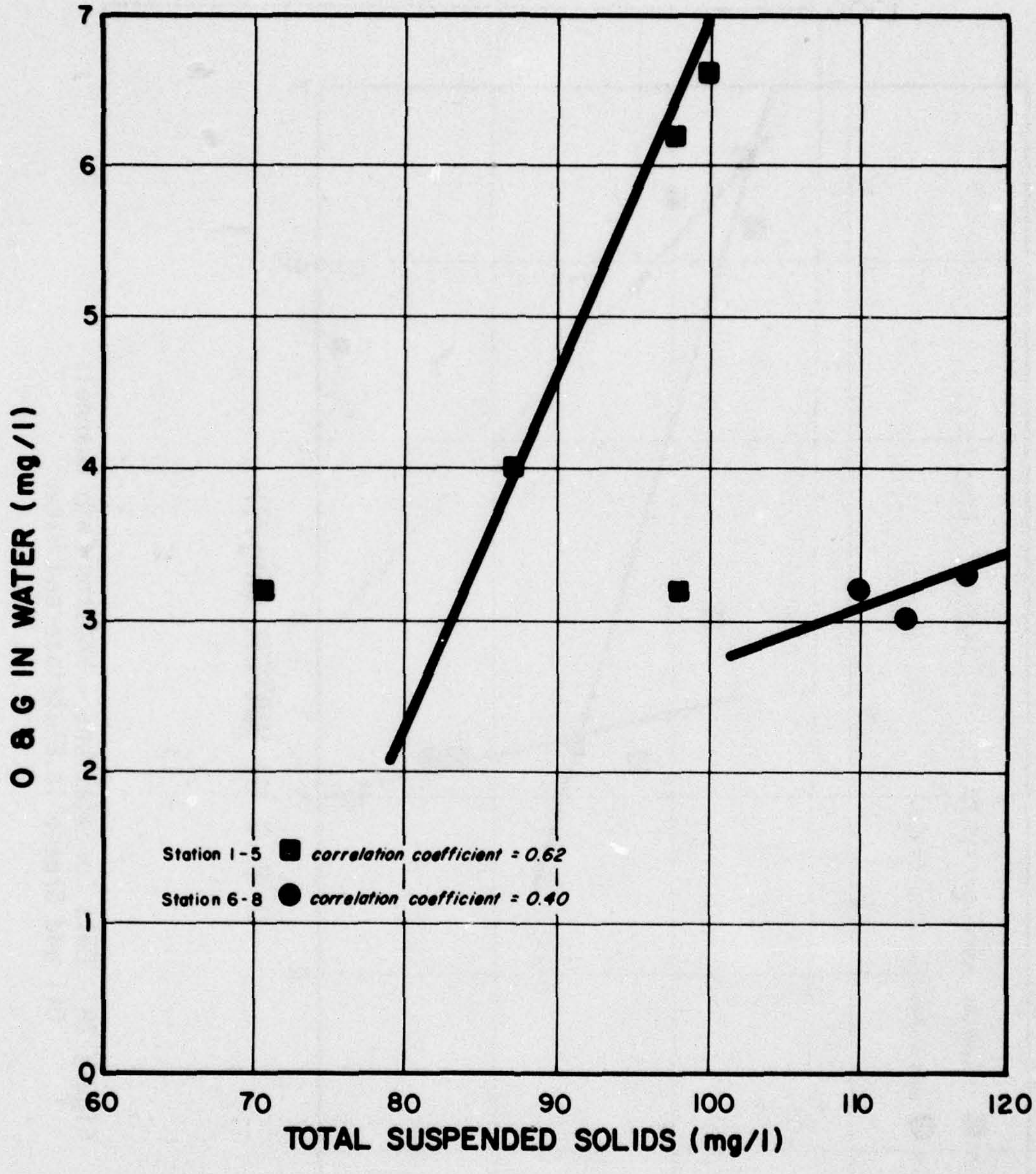

Figure 27. Data Correlations - Houston Ship Channel: Oil and Grease in Water and Total Suspended Solids

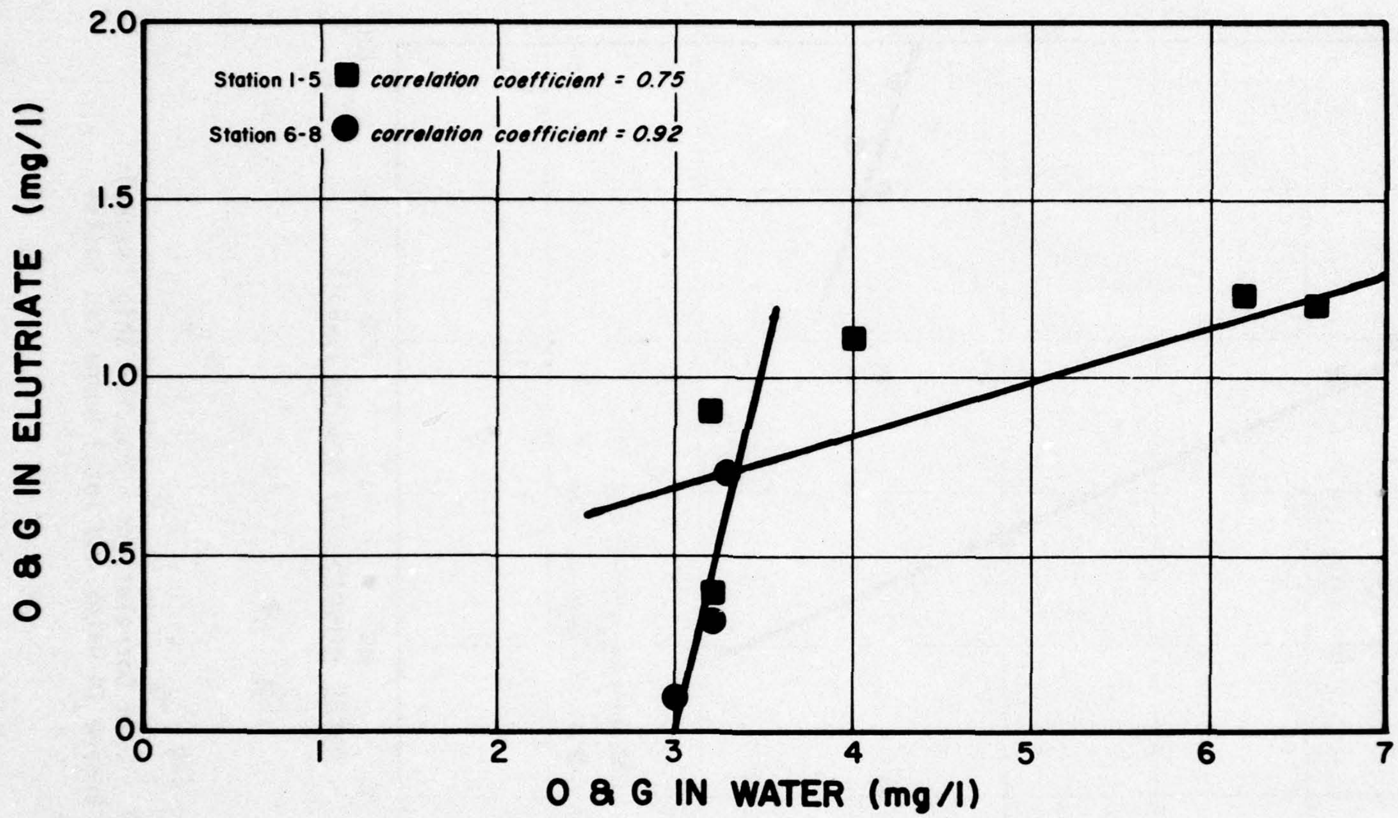

Figure 28. Data Correlations - Houston Ship Channel: Oil and Grease in Elutriate and Water

small and may not adequately characterize the population from which the samples were drawn. In fact, the elimination of a single data point (for good reasons such as atypical conditions at the site as compared to the remaining sites) can completely reverse the directionality of the best-fit linear regression line for a particular parameter. The sampling of multiphase systems, such as oil in water, is often a difficult task, and an additional margin for error is introduced when only single grab samples are taken.

161. Prior to conducting the field studies, it had been postulated that oil and grease would be associated with the sediments by adsorption and adhesion phenomena. Consequently, sediments composed of relatively small particles, having a high surface area per unit of volume, would display higher levels of oil and grease than coarser grained sediments. As is shown by the sign of the correlation coefficients presented in Table 24, this relationship was not consistently shown by the field study data.

162. The relationship between porosity and sediment oil and grease was also investigated. It was considered possible that oil and grease might be associated with interstitial water and that porosity would therefore be a factor in the level of oil accumulated in the sediments. The data, however, show no consistent relationship between porosity and sediment oil and grease content.

163. Two other relationships, as shown in Figures 27 and 28, were investigated. The first possible relationship, between suspended solids and oil and grease in the aqueous phase, was assessed to determine if oil and grease is consistently associated with suspended particles. The other relationship, between oil and grease in the diluent water and oil and grease in the elutriate, was investigated to determine if elutriate oil and grease levels are correlated to oil and grease levels in the dilution water used in the elutriate test. Consistent relationships for neither set of parameters were found in the field study data.

164. Attempts were made to correlate the amount of oil in the sediments and elutriate, as shown in Figure 29. Since each sediment

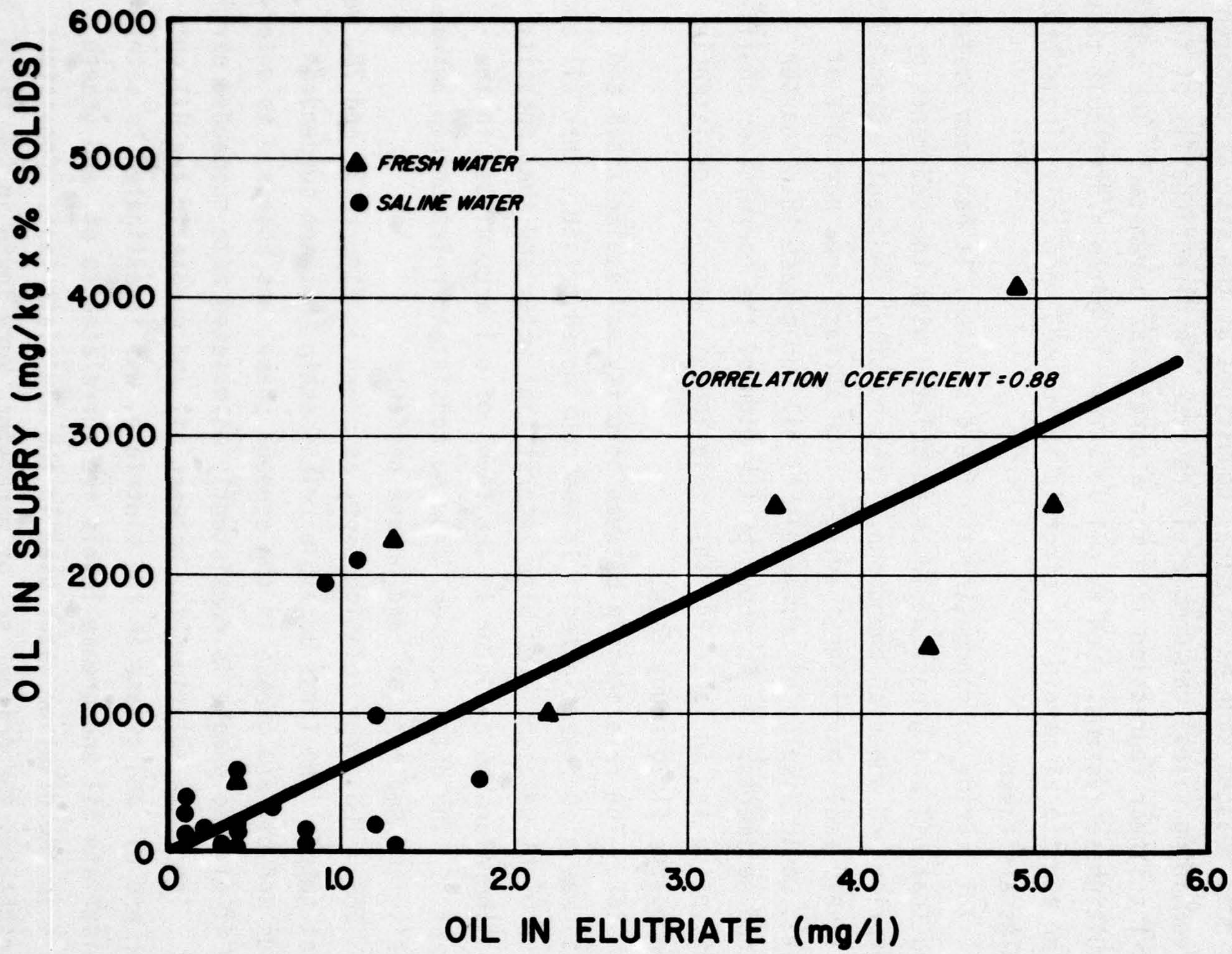

Figure 29. Correlation Between Oil in Sediment and Elutriate

sample had a different oil and grease and solids content, the actual sediment oil content was determined in order to obtain a common basis for comparison. This was accomplished by multiplication of the oil and grease content of the sediment (in mg/kg) by the solids content of the sediment (expressed as a fraction). As can be seen from Figure 29, some correlation can be found between the two variables. If the data were further divided into saline and fresh water groups, a better correlation might be obtained. The correlation between oil in the sediment and oil in elutriate from freshwater samples is shown in Figure 30.

165. Little correlation existed between oil in sediment and oil in the elutriate for samples collected at saline water sites. In fact, at almost all of the saline water sampling stations, the sediment elutriate contained lower concentrations of oil and grease than the water sample used in the test, indicating that oil was removed from the aqueous phase. This also occurred for several of the freshwater sediment samples, but the results were not so marked as for the saline waters. The field study data indicate that more oil tends to elutriate out of the sediment when fresh water is used in the test. This phenomenon is explainable by the well-known "salting-out" effect in which the solubility of certain solutes in a solvent may be reduced by the addition of salt. This finding raises doubt as to the utility of the elutriate test for predicting oil releases from dredged sediments, especially for saline waters.

166. Data collected at the three Houston Ship Channel dredged material containment areas can also be evaluated to determine the existence of relationships that can be used to predict oil concentrations in return flows as a function of various environmental factors. As shown in Figure 31, the average oil and grease level in the disposal site return waters correlates well with the oil levels in the sediments dredged, with a correlation coefficient of 0.99.

167. It appears that oil and grease and TSS in the return waters are also related. Figures 32 through 35 exhibit the regression analyses relating these two parameters. The statistical correlation coefficients for the Clinton and Jones Disposal Sites are shown as 0.67 and 0.76,

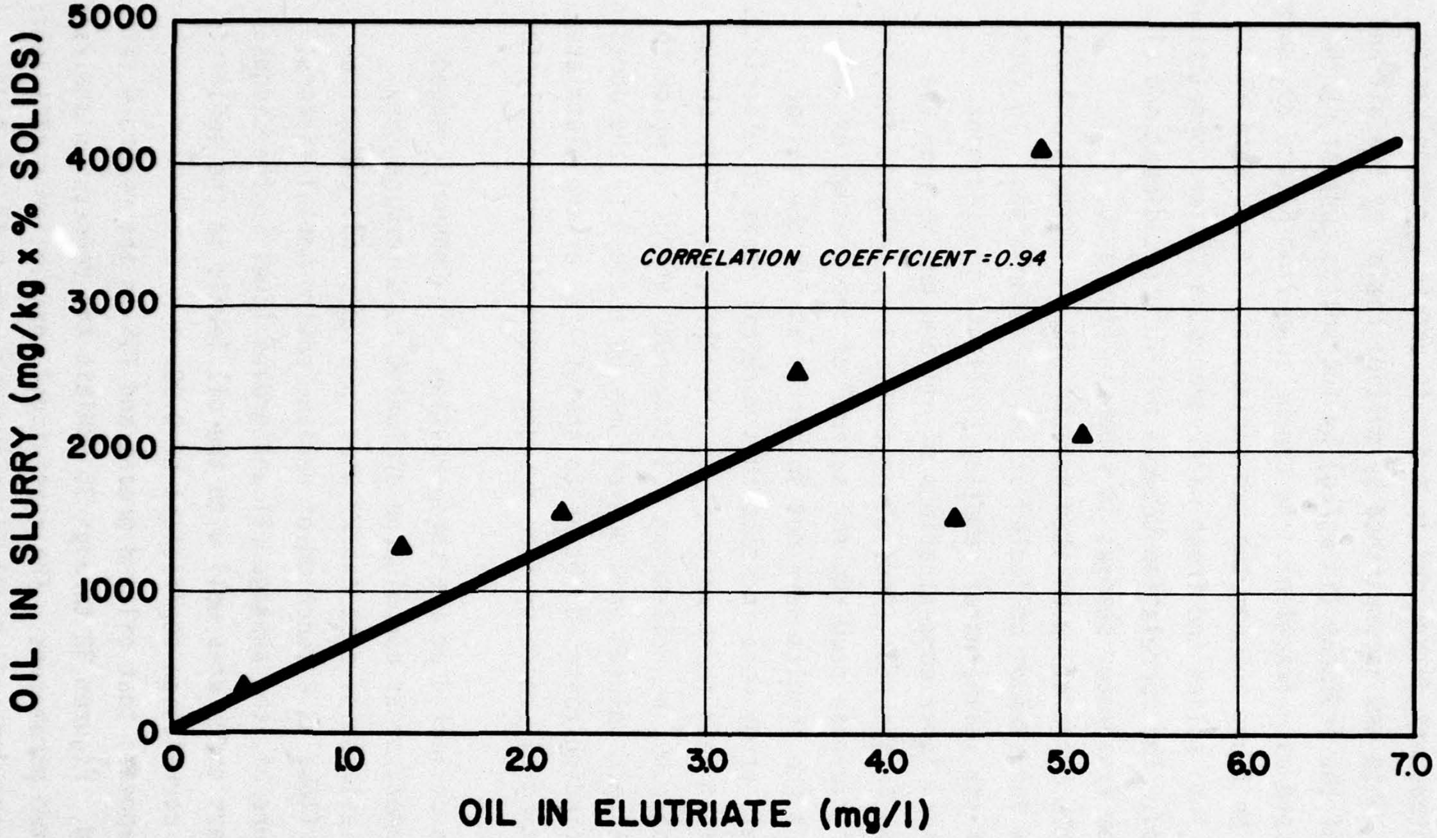

Figure 30. Correlation of Oil in Sediment and Elutriate for Freshwater Sites

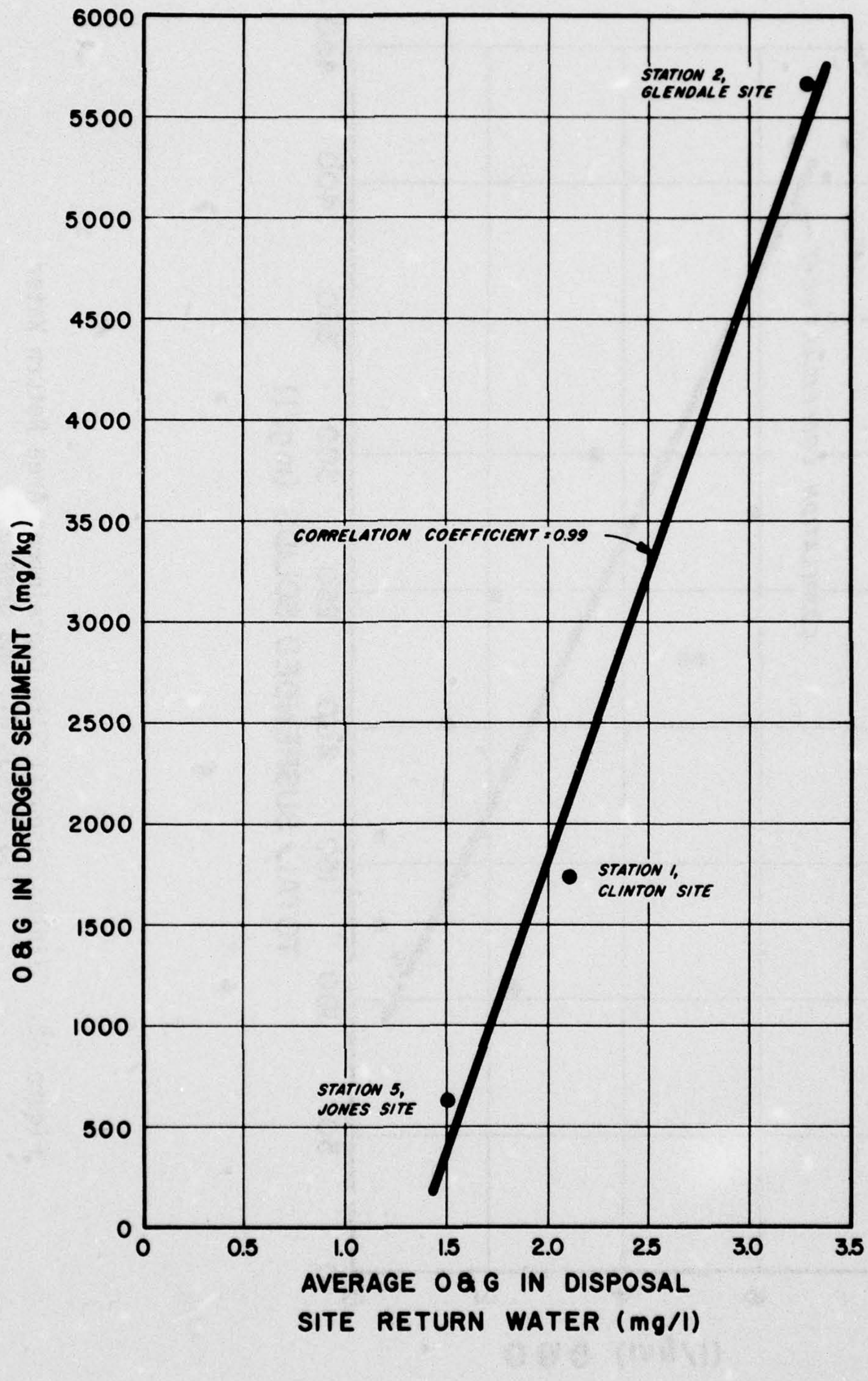

Figure 31. Correlation of Disposal Site Return Water and Source Sediment Oil and Grease Concentration Houston, Texas

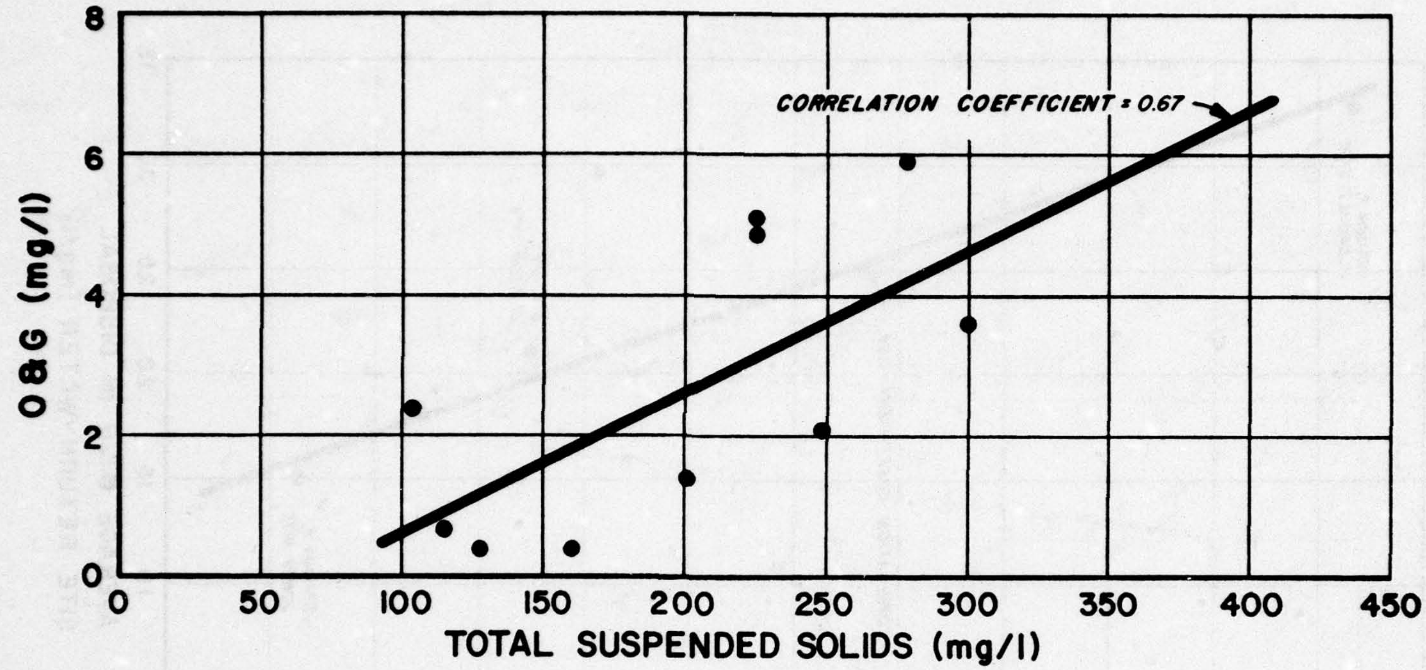

Figure 32. Clinton Disposal Site Containment Area Return Water
TSS versus Oil and Grease
Houston, Texas

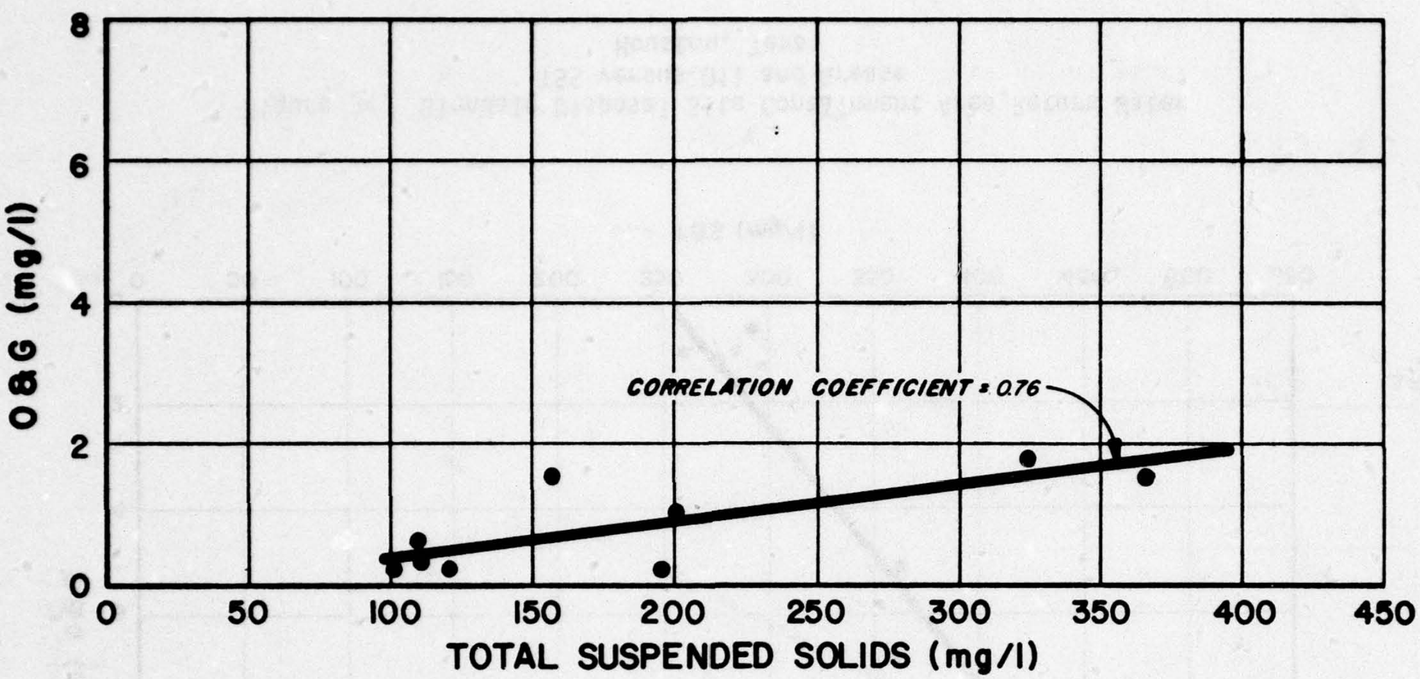

Figure 33. Jones Disposal Site Containment Area Return Water
TSS versus Oil and Grease
Houston, Texas

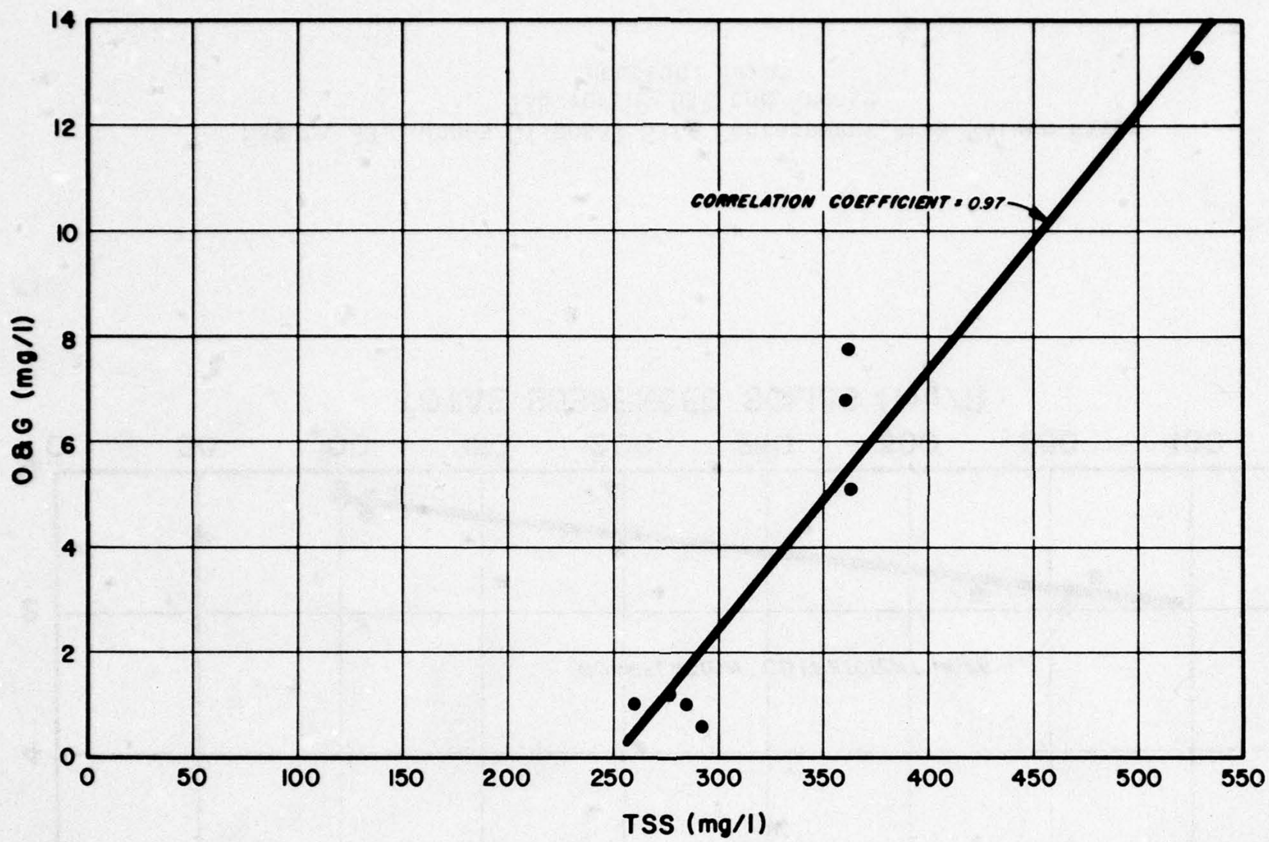

Figure 34. Glendale Disposal Site Containment Area Return Water
TSS versus Oil and Grease
Houston, Texas

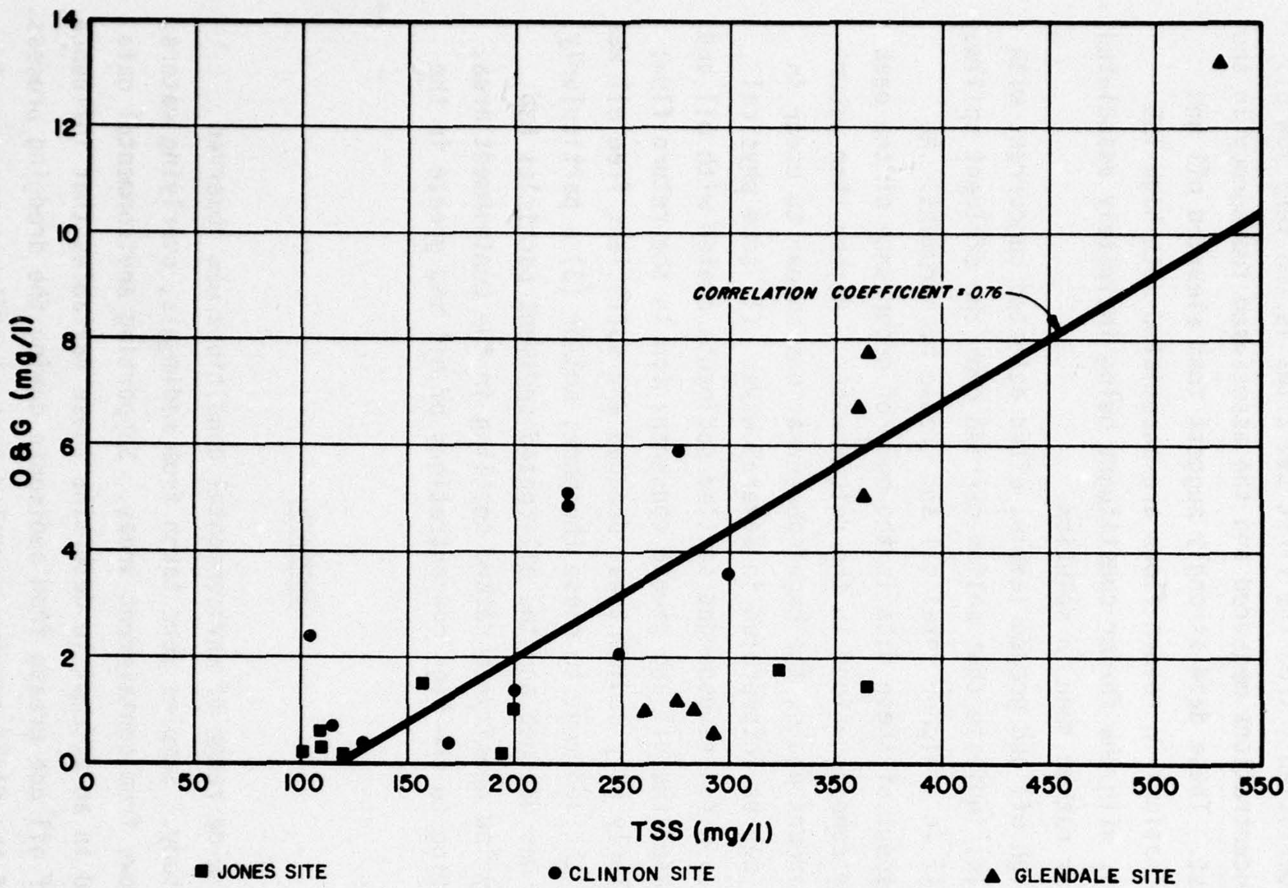

Figure 35. Glendale, Clinton, and Jones Disposal Sites Containment Area Return Water TSS versus Oil and Grease Houston, Texas

respectively. The data from the Glendale Site correlated better with a correlation coefficient of 0.97. One possible reason for the lower correlation coefficients from the first two sites is the very low oil and grease concentrations measured and the associated inaccuracy in the analytical test. These data strongly suggest that elevated oil and grease concentrations in return flows are associated with high TSS concentrations, with the former constituent being intimately associated with the latter rather than in solution.

168. High oil and grease levels, often detected concurrent with high TSS levels, indicate that solids carried over the effluent spillway probably result in a higher total oil and grease measurement. An interesting aspect of these data is the mode of occurrence of the peak oil and grease concentrations in the return water. Rather than occurring as independent peaks, the high concentrations appear to occur in groups. This can be interpreted in several ways: (1) some physical factor, such as wind, resuspended settled sediments coated with oil and thereby increased the oil and grease concentration in the return flow; (2) a particularly oily sediment was dredged and sufficient free oil was released from the sediment to cause the peak; and/or (3) a particularly oily sediment was dredged and the oil-coated sediment particles had a sufficiently low density to retard settling in the containment area, thus contributing to the high concentrations of oil and grease in the effluent.

Summary

169. A wide range of environmental conditions was observed during this study. Samples were taken from sediments, overlying waters, and return flows from containment areas. Supporting environmental data were collected in an attempt to determine those variables that influence the release of oil and grease from sediments during the dredging process. The results of the field surveys revealed that significant amounts of oil and grease do not appear to be released from sediments during the dredging process. Measured oil and grease concentrations in containment

area return flows were generally less than 5.0 mg/l. It is noted that at these concentrations, the analytical procedure for measuring oil and grease contains considerable variability and that measurements below this level should only be considered in a qualitative or comparative sense.

170. The highest oil and grease concentration measured during this study in containment area return flows was 13 mg/l. In terms of point-source discharges, this level would be considered low for a single maximum grab sample value. Point sources that discharge significant quantities of oil and grease are generally given permit limitations for single grab samples in the range of 15 to 25 mg/l of oil and grease. In comparison to point-source discharges, it can be concluded that containment area return flows are not a significant source of oil and grease discharge to most receiving waters.

171. As a complementary study during this project, a modified form of the standard elutriate test was used to determine the potential for the release of oil and grease from sediments during the dredging process. The results indicate that with the possible exception of freshwater environments, the modified form of the elutriate test is a poor predictor of oil and grease in return water from containment areas. In saline water, the oil and grease in the elutriate was actually less than the concentrations measured in the diluent water used in the test. This indicates that oil and grease was sorbed from the solution onto the sediments. A wide range of very oily sediments was studied and in almost all cases the maximum elutriate oil and grease concentrations from these sediments was below 5.0 mg/l. As discussed above, concentrations of oil and grease higher than this have occasionally been measured in containment area return flows. The results of the field studies indicated that most oil and grease in water samples and in return flows were associated with fine suspended sediments that were removed in the elutriate test. It is also possible that the mechanism of the test actually causes oil to be removed from solution and bound tightly to the sediment material. These possibilities are evaluated in greater depth in the bench-scale studies described in Part V of this report.

172. In summary, the results of the field survey portion of this project seem to indicate that oil and grease released from sediments during the dredging process are not a significant problem in terms of receiving water contamination. It appears that a properly designed containment area that removes the majority of the suspended material in the return flow will also remove the majority of the oil and grease.

173. A number of attempts were made to correlate oil and grease released from dredged sediments with various environmental parameters. No consistent relationships were found, although the elutriate test did seem to indicate that saline waters caused the oil and grease to be more tightly bound to the sediments than did fresh waters. This has been explained previously and is attributed to the so-called "salting-out" effect apparent in high-conductivity solutions. No other environmental parameter was found to strongly influence oil and grease release.

PART V: BENCH-SCALE STUDIES

Introduction

174. Bench-scale studies were conducted in order to confirm or refute the findings of the field survey, which indicated that oil and grease concentrations in return waters may be sufficiently low so that no treatment is required above and beyond that already provided by temporary containment. The bench-scale studies were designed to determine the significant chemical and physical factors that may affect the release of oil and grease from sediment during dredging operations.

175. All sediment samples were taken from the Houston/Galveston/Texas City area, where sediments exhibit a wide range of oil concentrations and particle-size distributions. The oil and grease concentrations in these sediments were presented in Table 5 (Part II).

176. The original outline of the bench-scale studies included plans for additional tasks found to be unnecessary based on the results of the initial experiments. It was planned to utilize the experimental data in the development of a predictive relationship using multiple regression methods for estimating the release of oil and grease from sediments. Data from the bench-scale studies, however, showed no consistent patterns or significant amounts of oil and grease release and a predictive relationship was not developed. Similarly, since the results of the bench-scale experiments showed that oil and grease could not be released from sediments in significant amounts under various conditions, an evaluation of the standard elutriate test and the development of an alternate laboratory method that could be used for predicting oil and grease releases from the sediment were not undertaken. The inability to effect the release of oil and grease from sediments under various environmental conditions obviated the need to conduct additional studies of treatment methods as planned.

Laboratory Procedures

177. The chemical and physical factors evaluated with regard to their effect on the release of oil and grease from sediments included shearing and centrifugal forces exerted on the sediment/water slurry as it passes through the dredge pump impeller, oil content of the sediment, particle-size distribution, salinity, temperature, and pH. Prior to running the experiments, it was believed that the major factors that might influence oil release from the sediment during dredging were shearing and centrifugal forces of the pump used in hydraulic dredging. Since the bucket-type dredge agitates the sediments much less than the hydraulic dredge, it was believed that study of the physical conditions associated with hydraulic dredging would provide a conservatively high estimate of the potential for oil release during dredging.

178. The experimental procedure, depicted in Figure 36, was designed to identify the factors potentially affecting the processes by which oil and grease are released from sediments. In the first step of the procedure, a particular set of conditions (i.e., pH, temperature, salinity, and mixing rate) was selected and held constant while a single factor (i.e., time of circulation) was varied. The level of the variable factor that resulted in the greatest release of oil and grease was then used in the next series of experiments and another factor (i.e., mixing rate) was varied, with all other factors held constant. Repeating this process for each sample until every factor had been varied, the resulting set of conditions should have represented conditions under which the greatest release of oil and grease could be achieved.

179. In each analysis, the original partitioning ratio of one part sediment to four parts water was utilized so as to evaluate only the release mechanisms and not the extraction efficiency of different ratios of water to sediment.

180. All laboratory procedures utilized a simple apparatus consisting of a small centrifugal pump circulating the slurry through a two-l aspirator bottle. The time of circulation refers to the length

STEP I

Determine time of circulation that yields highest elutriate oil concentration:

Constants: pH, temperature, salinity, impeller speed
Variable: time of circulation (range: 5-15 min)

STEP II

Determine impeller speed that yields highest elutriate oil concentration:

Constants: pH, temperature, salinity, time of circulation
Variable: impeller tip speed (range: 2.9-7.8 m/sec)

STEP III

Determine salinity that yields highest elutriate oil concentration:

Constants: pH, temperature, time of circulation, impeller speed
Variable: salinity (range: 0-25 ppt)

STEP IV

Determine pH that yields highest elutriate oil concentration:

Constants: temperature, time of circulation, impeller speed, salinity
Variable: pH (range: 6-10)

STEP V

Determine temperature that yields highest elutriate oil concentration:

Constants: time of circulation, impeller speed, salinity, pH
Variable: temperature (range 10-30°C)

REPEAT EXPERIMENTAL PROCESS WITH NEXT SAMPLE

Figure 36. Experimental Procedure

of time the mixture was circulated through the apparatus. Following this mixing step, the sediment/water mixture was allowed to settle for 24 hr, at which time the oil and grease concentration in the supernatant was determined. A 24-hr settling period was utilized since observations from the field studies indicated that a greater concentration of oil and grease would be detected than if the sample were centrifuged.

181. The rate of mixing was varied by regulation of the voltage applied to the pump by means of a variable transformer. The stall speed of the pump set the lower limit of the mixing rate. Pump speed was determined using a stroboscopic tachometer. Mixing rates were adjusted so that the tip speed of the pump impeller was in the range of that of centrifugal pumps used in the dredging process. Obviously, clamshell-type dredges are not simulated with this technique.

182. Salinity was varied from 0 to 25 ppt by addition of sodium chloride. The initial expectation was that as the salinity (and resultant polarity of the extracting water) increased, the oil and grease release, particularly the nonpolar release, would decrease.

183. The pH variance was measured as a function of the pH of the resultant mixture. If water of a particular and adjusted pH were added to the sediment and the test begun immediately, the test would be dependent upon the buffering capacity of the sediment. For this reason, the water and sediment were combined and the pH adjusted to a final value with nitric acid or sodium hydroxide. Hydrochloric acid was not used, as it was desired not to alter the chloride concentration. pH values covered the range of 6.0 (possible in natural waters) to 10 (highly unlikely in natural waters) standard units. It is possible that at pH 10 some of the oil and grease had been saponified and thus not measured in the test. This possible effect was not investigated and data are presented as measured directly from solvent extraction.

184. Although classic reaction kinetics do not predict a significant difference in the physical and chemical reactions between the sediment and the elutriate over a 20°C spread, temperatures ranging from 10°C to 30°C were tested. Within this temperature range, many of the greases that are extracted will change from solid to liquid form,

and this is important since the ability of the grease to interact is enhanced by its liquidity. In addition, the ability or inability to form various emulsions is dependent upon small temperature increments.

185. Sediment samples were analyzed for their oil and grease content (presented in Table 5 of Part II).

Data Summary and Evaluation

186. The results of the bench-scale experiments are presented in Tables 25 through 28 and graphical summaries are depicted in Figures 37 through 41. The conditions under which the tests were conducted are shown in each figure. The figures are grouped in five categories, these being the analyses with the same variable factor (i.e., temperature, pH, etc.). Mean values of the multiple analyses of both total and nonpolar oil and grease are shown in the figures. Again, the results must be evaluated with due regard for the analytical variability of the oil and grease test discussed in Part II.

187. A cursory review of the figures is sufficient to reveal that the release of oil and grease from sediments did not demonstrate a consistent pattern for any chemical or physical factor. For example, with increasing salinity samples PA-2 and HSC-8, as expected, showed lower levels of oil and grease in the supernatant, however, samples PA-1 and HSC-3 showed higher oil and grease concentrations.

188. It is notable that the supernatant oil and grease concentrations measured in the final set of tests for each sample are not greatly different from the preceding measurements. It had been expected that the maximum supernatant concentrations would increase somewhat (or at least remain constant) in each step of the experimental process, but this was not consistently observed. In fact, the maximum supernatant oil concentration measured in any particular step of the experimental process actually decreased as often as it increased from the maximum value found in the preceding step.

189. Regardless of sediment oil concentration and the conditions tested, oil and grease concentrations in the supernatant were quite low,

Table 25

Results of Bench-scale Tests for Sample PA-1

Test Conditions	Temperature °C	Total Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Nonpolar Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Percent Nonpolar Oil
Variance with time, min								
5	24.5	8.3/4.7	6.5	2.54	7.8/3.6	5.7	2.96	88
10	25.0	7.7/7.5	7.6	0.14	4.9/5.1	5.0	0.14	66
15	27.0	6.7/4.7	5.7	1.41	6.3/4.7	5.5	1.13	96
Variance with impeller speed (Time = 10 min)								
7.8 m/sec	24.3	4.8/6.2/7.4	6.1	1.30	2.4/2.9/2.3	2.5	0.32	41
7.4 m/sec	24.7	4.5/2.9/3.4	3.6	0.82	2.6/1.6/1.5	1.9	0.61	53
6.9 m/sec	24.7	2.0/2.3/1.3	1.9	0.51	0.8/1.9/1.3	1.3	0.55	68
2.9 m/sec	24.3	4.6/5.4/4.6	4.9	0.46	1.9/1.5/1.3	1.6	0.31	33
Variance with salinity (Time = 10 min) (Impeller speed = 7.8 m/sec)								
0 ppt	24.3	4.8/6.2/7.4	6.1	1.30	2.4/2.9/2.3	2.5	0.32	41
15 ppt	24.3	17.4/6.0/10.7	11.4	5.73	5.3/4.0/4.4	4.6	0.66	40
25 ppt	25.7	9.7/12.8/4.8	9.1	4.03	7.1/5.0/3.1	5.1	2.00	56
Variance with pH (Time = 10 min) (Impeller speed = 7.8 m/sec) (Salinity = 15 ppt)								
pH = 6	23.0	3.8/2.8/3.5	3.4	0.51	1.5/1.4/1.6	1.5	0.10	44
pH = 7	23.0	6.1/12.2/8.7	9.0	3.06	3.1/5.3/3.4	3.9	1.19	43
pH = 10	23.7	12.2/9.6/9.5	10.4	1.53	3.7/0.8/0.9	1.8	1.65	17
Variance with temperature, °C (Time = 10 min) (Impeller speed = 7.8 m/sec) (Salinity = 15 ppt) (pH = 7)								
10	10.0	4.7/4.9/4.2	4.6	0.36	2.6/2.3/1.1	2.0	0.79	43
15	15.0	5.4/7.4/5.0	5.9	1.28	4.4/4.4/4.0	4.3	0.23	73
23.5	23.5	4.9/5.2/3.6	4.6	0.85	0.8/0.8/0.8	0.8	0.00	17
30	30.0	4.8/5.4/5.1	5.1	0.30	3.2/2.8/3.0	3.0	0.20	59

* Multiple analyses.

Note: PA-1 - sample site 1 on the Sabine-Neches Canal, Port Arthur, Texas.

Table 26

Results of Bench-scale Tests for Sample PA-2

Test Conditions	Temperature °C	Total Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Nonpolar Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Percent Nonpolar Oil
Variance with time, min								
5	23.0	1.9/3.7	2.8	1.27	---	---	---	---
10	23.0	1.6/3.5	2.5	1.34	---	---	---	---
15	24.5	2.8/5.5	4.1	1.91	---	---	---	---
Variance with impeller speed (Time = 10 min)								
7.8 m/sec	25.8	3.5/3.8/2.2	3.2	0.85	1.4/1.9/2.0	1.8	0.32	56
7.4 m/sec	25.2	1.9/4.7/2.9	3.2	1.42	3.3/2.2/3.6	3.0	0.74	94
6.9 m/sec	23.5	7.4/3.6/7.5	6.2	2.22	2.4/2.0/2.5	2.3	0.26	37
2.9 m/sec	24.0	6.1/5.5/8.3	6.6	1.47	2.5/3.3/2.6	2.8	0.44	42
Variance with salinity (Time = 10 min) (Impeller speed = 6.9 m/sec)								
0 ppt	23.5	7.4/3.6/7.5	6.2	2.22	2.4/2.0/2.5	2.3	0.26	37
15 ppt	22.8	5.2/3.4/3.5	4.0	1.01	3.6/2.8/2.5	3.0	0.57	75
25 ppt	23.0	2.4/2.6/3.9	3.0	0.81	1.2/1.3/2.4	1.6	0.67	54
Variance with pH (Time = 10 min) (Impeller speed = 6.9 m/sec) (Salinity = 0 ppt)								
pH = 6	24.5	1.0/0.9/3.9	1.9	1.70	0.5/0.5/0.7	0.6	0.12	32
pH = 7.4	23.5	7.4/3.6/7.5	6.2	2.22	2.4/2.0/2.5	2.3	0.26	37
pH = 8.0	24.5	1.8/2.9/0.3	1.6	1.30	1.2/1.4/0.3	1.0	0.59	62
pH = 10	22.2	0.8/1.8/0.8	1.1	0.58	0.9/0.5	0.7	0.28	64
Variance with temperature, °C (Time = 10 min) (Impeller speed = 6.9 m/sec) (Salinity = 0 ppt) (pH = 7.4)								
10	10.0	1.5/0.4/1.2	1.0	0.57	0.7/0.4/1.0	0.7	0.30	70
15	15.0	13.2/8.5/3.0	8.2	5.10	4.2/6.5/1.9	4.2	2.30	51
23.5	23.5	7.4/3.6/7.5	6.2	2.22	2.4/2.0/2.5	2.3	0.26	37
30	30.0	1.4/1.6/1.2	1.4	0.20	0.6/1.2/0.6	0.8	0.35	57

* Multiple analyses.

Note: PA-2 - Sample site 2 on the Sabine-Neches Canal, Port Arthur, Texas.

Table 27

Results of Bench-scale Tests for Sample HSC-3

Test Conditions	Temperature °C	Total Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Nonpolar Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Percent Nonpolar Oil
Variance with time, min								
5	20.5	3.4/7.9	5.6	3.2	---	---	---	---
10	23.8	2.5/4.8	3.6	3.0	---	---	---	---
15	26.0	6.3/3/0	4.6	2.3	---	---	---	---
Variance with impeller speed (Time = 10 min)								
7.8 m/sec	24.0	2.8/2.3/5.8	3.6	1.89	2.0/1.4/3.7	2.4	1.19	67
7.4 m/sec	24.3	2.9/2.4/1.9	2.4	0.50	1.6/0.9/1.0	1.2	0.38	50
6.9 m/sec	24.0	2.3/2.0/3.3	2.5	0.68	1.4/0.9/0.9	1.1	0.29	44
2.9 m/sec	23.7	2.7/2.4	2.6	0.21	1.8/0.6	1.2	0.72	57
Variance with salinity (Time = 10 min) (Impeller speed = 7.8 m/sec)								
0 ppt	24.0	2.8/2.3/5.8	3.6	1.89	2.0/1.4/3.7	2.4	1.19	67
15 ppt	21.5	3.3/3.2/1.9	2.8	0.78	0.9/0.9/0.6	0.8	0.17	29
25 ppt	22.2	5.0/1.6/9.5	5.4	3.96	1.7/0.9/5.2	2.6	2.29	48
Variance with pH (Time = 10 min) (Impeller speed = 7.8 m/sec) (Salinity = 25 ppt)								
pH = 6	20.0	3.5/4.2/3.3	3.7	0.47	1.5/2.3/1.5	1.8	0.46	49
pH = 7.5	22.0	5.0/1.6/9.5	5.4	3.25	1.7/0.9/5.2	2.6	2.29	48
pH = 8	20.3	3.1/4.9/2.4	3.5	1.29	1.5/3.2/1.4	2.0	1.01	57
pH = 10	19.7	8.3/5.6/4.3	6.1	2.04	3.9/2.8/2.6	3.1	0.70	51
Variance with temperature, °C (Time = 10 min) (Impeller speed = 7.8 m/sec) (Salinity = 25 ppt) (pH = 10)								
10	10.0	3.6/2.7/2.4	2.9	0.62	2.2/2.1/1.5	1.9	0.38	67
15	15.0	13.2/4.9/6.7	8.3	4.40	4.0/2.2/2.9	3.0	0.90	44
20	20.0	8.3/5.6/4.3	6.1	2.04	3.9/2.8/2.6	3.1	0.70	51
30	30.0	3.8/2.2/2.9	3.0	0.80	2.7/1.2/1.4	1.8	0.81	60

*Multiple analyses.

Note: HSC-3 - Sample site 3 on the Houston Ship Channel.

Table 28

Results of Bench-scale Tests for Sample HSC-8

Test Conditions	Temperature °C	Total Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Nonpolar Oil and Grease* mg/l	Mean mg/l	Standard Deviation	Percent Nonpolar Oil
Variance with time, min								
5	22.0	1.5/2.2	1.8	0.5	1.0	---	---	56
10	22.8	9.4/9.3	9.4	0.7	1.0	---	---	11
15	25.8	3.1/3.6	3.4	0.35	1.0	---	---	29
Variance with impeller speed (Time = 10 min)								
7.8 m/sec	24.0	2.3/4.0/0.5	2.3	1.75	1.1/2.0/0.4	1.2	0.80	52
7.4 m/sec	23.3	2.3/1.8/2.0	2.0	0.25	1.3/1.0/1.3	1.2	0.17	60
6.9 m/sec	21.8	5.6/5.2/3.7	4.8	1.00	4.3/2.1/1.1	2.5	1.64	52
2.9 m/sec	20.8	6.3/2.2/2.9	3.8	2.19	1.7/0.7/1.0	1.1	0.51	29
Variance with salinity (Time = 10 min) (Impeller speed = 6.9 m/sec)								
0 ppt	21.8	5.6/5.2/3.7	4.8	1.00	4.3/2.1/1.1	2.5	1.64	52
15 ppt	21.8	1.4/0.8/2.3	1.5	0.75	0.5/0.5/0.9	0.6	0.23	40
25 ppt	22.3	2.1/2.6/2.3	2.3	0.25	0.9/0.9/0.6	0.8	0.17	35
Variance with pH (Time = 10 min) (Impeller speed = 6.9 m/sec) (Salinity = 0 ppt)								
pH = 6	20.0	2.0/1.5/2.2	1.9	0.36	1.2/0.9/1.0	1.0	0.15	55
pH = 7	19.7	3.1/3.1/3.1	3.1	0.00	2.1/1.2/1.8	1.7	0.46	55
pH = 7.9	21.8	5.6/5.2/3.7	4.8	1.00	4.3/2.1/1.1	2.5	1.64	52
pH = 10	19.7	2.9/2.8/9.1	4.9	3.60	1.5/1.3/2.9	1.9	0.87	50
Variance with temperature, °C (Time = 10 min) (Impeller speed = 6.9 m/sec) (Salinity = 0 ppt) (pH = 7)								
10	10.0	4.2/2.4/0.9	2.7	1.76	1.5/0.5/0.4	0.8	0.61	31
15	15.0	0.7/0.8/0.7	0.7	0.06	0.4/0.6/0.2	0.4	0.20	57
19.7	19.7	3.1/3.1/3.1	3.1	0.00	2.1/1.2/1.8	1.7	0.46	55
30	30.0	0.4/1.6/1.0	1.0	0.31	0.0/0.4/0.4	0.3	0.23	30

* Multiple analyses.

Note: HSC-8 - Sample site 8 on the Houston Ship Channel.

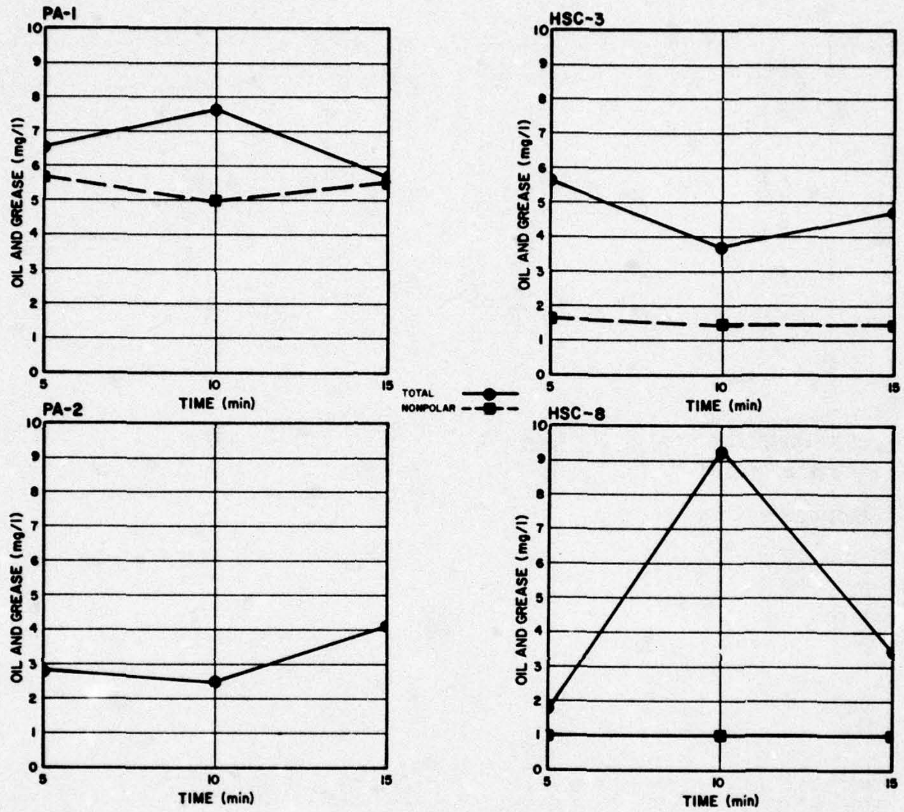

Figure 37. Oil and Grease Concentration
as a Function of Time of Circulation

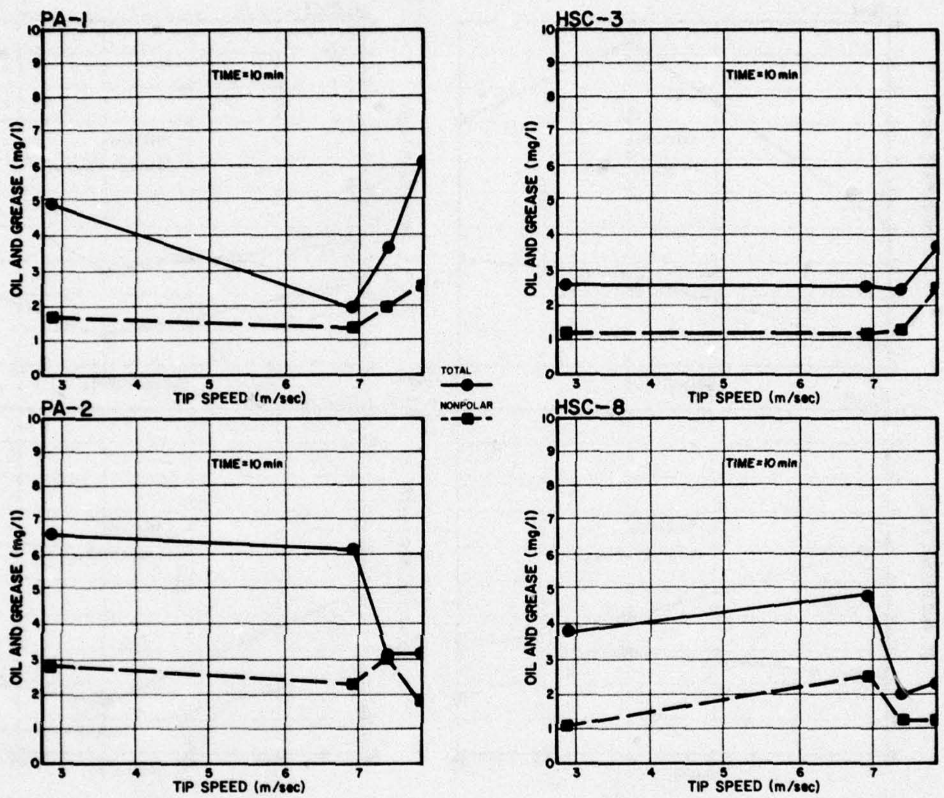

Figure 38. Oil and Grease Concentration as a Function of Impeller Speed

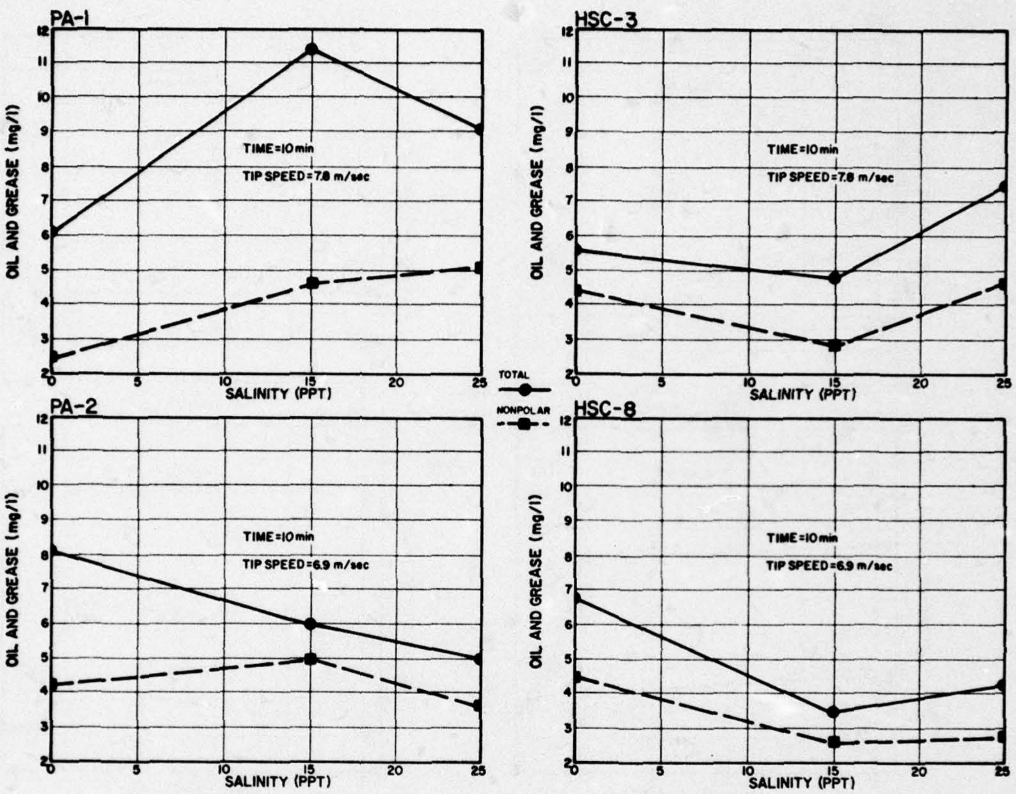

Figure 39. Oil and Grease Concentration
as a Function of Salinity

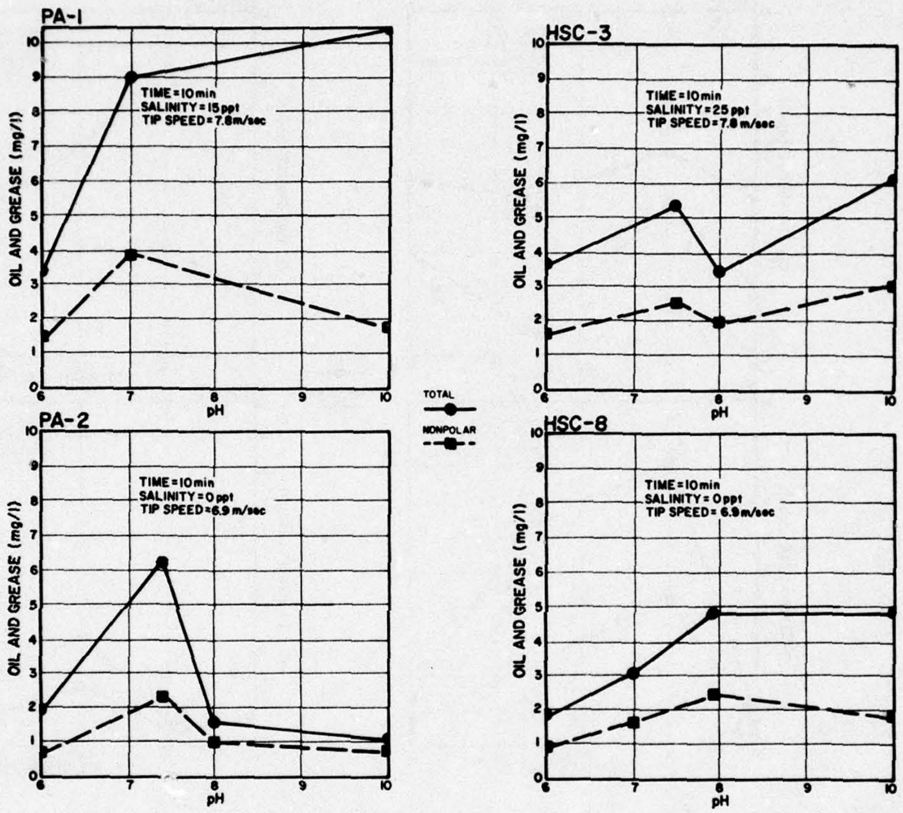

Figure 40. Oil and Grease Concentration as a Function of pH

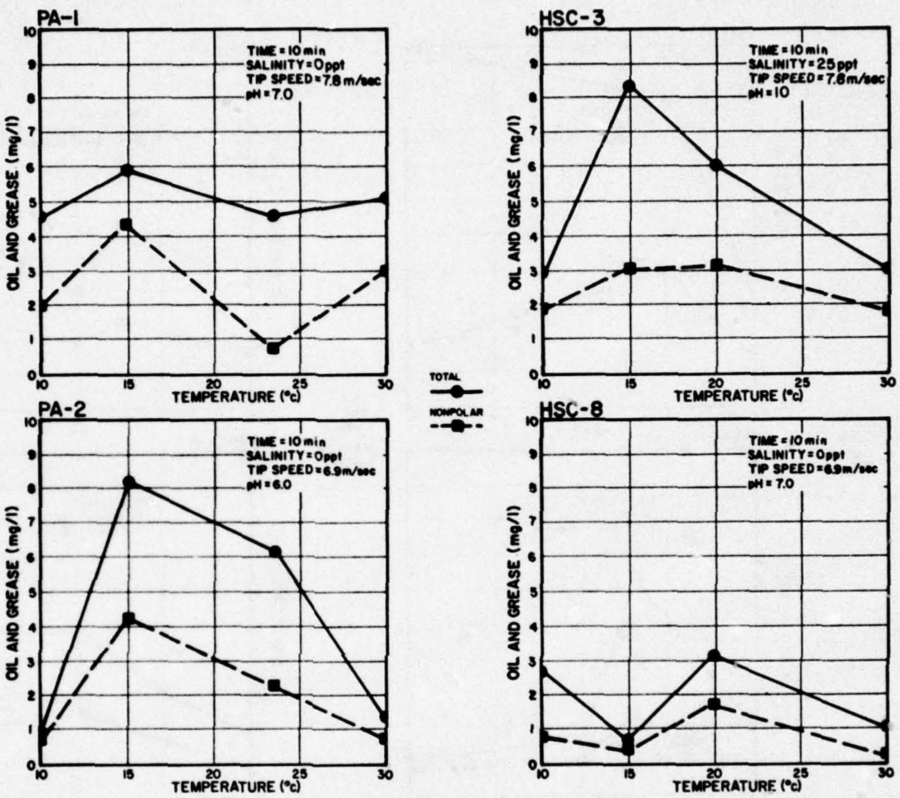

Figure 41. Oil and Grease Concentration as a Function of Temperature

indicating an extremely low release of oil and grease from the sediments. Only five out of 56 samples analyzed for total oil and grease had concentrations greater than 10 mg/l, and only one sample was greater than 15 mg/l (17.4 mg/l). This is in spite of the fact that one of the sediments contained three percent oil by weight. The significance of these low levels is apparent when one considers that the typical maximum grab sample limit for oil and grease in point-source discharges is 15 mg/l. In addition, these results are significant since the cost-effectiveness of removing oil and grease at levels of less than 20 mg/l is extremely poor and the performance of the applicable treatment processes is highly variable.

190. It can be concluded that it is very unlikely that significant quantities of oil and grease will be released to the aqueous phase during dredging under the normal range of physical and environmental conditions that can be expected. As discussed in the evaluation of the field study results, relatively high levels of oil and grease in containment area return waters, if they do occur, would be associated with the carryover of oil sorbed onto the surface of suspended particles and not from oil released to the aqueous phase.

PART VI: CONCLUSIONS

191. Based on the results of field surveys at six selected dredging sites and bench-scale laboratory studies, the following conclusions were derived from this investigation:

a. Oil and grease associated with sediments is not released to any significant extent by the dredging process under the expected environmental conditions that would be found at typical areas where maintenance dredging is practiced. The high concentrations of oily materials which are often measured in sediments, consist principally of substances that are tightly bound to the sediment particles. This is not unexpected since oils are generally lighter than water and would not be expected to be found in sediments unless they had been associated with particles that are heavier than water.

b. Because the oil and grease associated with most sediments cannot be easily released during the dredging process, oil and grease contamination from dredged material disposal areas does not appear to be a significant problem if the disposal area is properly confined and the spillway structure is carefully designed.

c. At the extremely low oil and grease concentrations measured in most of the aqueous samples collected during this study, both in the field and bench-scale tests, the analytical procedure is relatively imprecise. In other words, at oil and grease concentrations below 10 mg/l, the inherent variability in the analytical procedure is such that any correlations between environmental variables and oil concentrations are likely to be masked.

d. A correlation was found between the mean oil and grease concentration in return waters and the oil content in dredged sediments from three dredged material containment areas. However, the oil and grease concentration also correlated well with the total suspended solids concentrations in the return flow, thus supporting the above two conclusions.

e. Some correlation was found between oil levels in sediments and their elutriates in the samples taken at the fresh water dredging sites. However, the elutriate test, as modified for this investigation, did not work effectively on saline water and the correlations developed from the three dredged material containment

areas did not provide a cause-effect relationship that was useful to predict the oil and grease content of return flows.

f. Some modified elutriate test results showed less oil in the elutriate than was present in the diluent water used in the test. This result indicates that oil in the water may be adsorbed on the sediment particles instead of oil in the sediment being released to the water. In other words, it is possible that the dredging process may actually remove free oil from the water by allowing greater contact with sediment particles. It is also possible that oil in the tested water may be associated with solids separated from the water by centrifugation in the modified elutriate test.

g. Because of the extremely low oil and grease concentrations that occurred in the return flow and the results of the tests that show significant quantities of oil and grease are not released to the aqueous phase during the dredging process, it is infeasible to consider use of end-of-pipe treatment processes specifically designed to remove these substances from return flows. If necessary, emphasis should be upon improving performance of dredged material disposal areas in terms of suspended solids removal. Removal of fine suspended solids particles, based on the results of this study, will ensure that oil and grease concentrations in the return flows are at acceptable limits.

REFERENCES

1. Anon., "Man's Impact on the Global Environment," MIT Press, Cambridge, Mass., 1970, p 267.

2. Anon., "EPA Interim Regulations on Discharge of Dredged and Fill Material into Navigable Waters," Federal Register, 40 CFR Part 230, Washington, D.C., September 1975.

3. Anon., Water Quality Criteria, 1972, A report to the Committee on Water Quality Criteria, Environmental Studies Board, National Academy of Sciences, National Academy of Engineering, Washington, D.C. 1972 (at the request of and funded by the EPA).

4. Anon., "EPA Effluent Guidelines for Petroleum Refining," Federal Register, 40 CFR Part 419, Washington, D.C., September 1974.

5. Forster, R.L., et al, "Port Collection and Separation Facilities for Oily Wastes," Report to the U.S. Department of Commerce Maritime Administration, Volume 1, March 1973.

6. Anon., ASTM Standard Methods for Sampling Waters, Method D510-68.

7. Anon., "EPA Regulations on Test Procedures for the Analysis of Pollutants," Federal Register, 40 CFR Part 136, Washington, D.C., December 1976.

8. Chanin, G., et al, "A Safe Solvent for Oil and Grease Analysis," Journal of the Water Pollution Control Federation, Vol. 39, No. 11, November 1967, p 1892.

9. Anon., "EPA Regulations and Criteria for Ocean Dumping," Federal Register, 40 CFR Part 227, Washington, D.C., January 1977.

10. Personal communications with Dr. Milton Tunzi, U.S. Environmental Protection Agency, Alameda (Calif.) Laboratory, February 11, 1977.

11. Ford, D.L., and H. Azad, Editor in Chief, Chapter 8, "Water Pollution Control in the Petroleum Industry," Industrial Wastewater Management Handbook, McGraw-Hill, New York,, 1976.

12. Brown & Root, "Determination of Best Practicable Control Technology Currently Available to Remove Oil from Water Produced with Oil and Gas," Report to Sheen Technical Subcommittee and Offshore Operators Committee of the American Petroleum Institute, March 1974.

13. Peoples, R.F., et al, "Non-biological Treatment of Refinery Wastewater," Journal Water Pollution Control Federation, Vol. 44, No. 11, 1972, p. 2120.

14. Nebolsine, R., "New Methods for the Treatment of Oily Wastewater Streams," 25th Industrial Waste Conference, May 1970, p. 885.

15. Wallace, J.T., Jr., and J.S. Brown, "Deep Bed Filtration of Oil-field Produced Water," 27th Purdue Industrial Waste Conference, May 1972, p. 151.

16. Humenick, M.J., et al, "High Rate Filtration of Solid-stabilized Oil-in-Water Emulsion," Center for Research in Water Resources Report 105, University of Texas, Austin, Texas, 1973.

17. Beavon, D.K., "Sand Filtration Cuts Pollution," Oil and Gas Journal, June 1969.

18. Martinez-Pereda, P., and E.F. Gloyna, "Removal of Emulsified Oils in Graphite Ore Medium," Center for Research in Water Resources Report 118, University of Texas, Austin, Texas, 1975.

19. Smedley, J.B., et al, "Grease Removal with a Precoat Filter, A Case History," 29th Purdue Industrial Waste Conference, May 1974, p. 740.

20. Pursell, W.L., and R.B. Miller, "Waste Treatment of Skelly Oil Company's El Dorado, Kansas Refinery," 16th Purdue Industrial Waste Conference, 1961, p. 292.

21. Geyer, L.C., "Waste Treatment at Link-Belt's Ball and Roller Bearing Plant," 15th Purdue Industrial Waste Conference, March 1960.

22. Madarasz, M.F., "Pilot Plant Recovery of an Iron Coagulant from Oil Waste Treatment Sludge," 14th Purdue Industrial Waste Conference, September 1959, p 191.

23. Hasegawa, T., "Treating Wastewater of Water-Soluble Cutting Oils," Japan, Kokai, 74101059, January 1974.

24. Heutsched, M.L., and T.L. Cox, "Effluent Water Treating at Charter International Oil Company's Houston Refinery," 74th Annual American Institute of Chemical Engineers Meeting, New Orleans, 1973.

25. Anon., "Experimental Evaluation of Fibrous Bed Coalescers for Separating Oil-Water Emulsions," U.S. EPA Water Pollution Control Research Series, 12050-DRC-11/71.

26. Chieu, J.N., et al, "Coalescence of Emulsified Oily Wastewater by Fibrous Beds," Presented at the 30th Purdue Industrial Waste Conference, May 1975.

27. Caswell, C.A., "Use of Bacterial Cultures to Control Oily Wastewaters from a Bulk Oil Handling Terminal," 26th Purdue Industrial Waste Conference, May 1971, p. 1020.

28. McCrodden, B.A., "Water Pollution Abatement at BP Oil Corporation's Marcus Hook Refinery," 46th Annual Conference, Water Pollution Control Federation, October 1973.

29. Weber, W.J., Jr., "Physiochemical Processes for Water Quality Control," Wiley-Interscience, 1971.

30. Koizumi, S., "Removal of Oil from Water," Japan, Kokai, 72/42,384, December 1972, Appl. 71/30,587, May 1971.

31. Shinoda, K., et al, "Removal of Oils from Wastewater," Japan, Kokai, 74, 81075, August 1974.

32. Tamaki, K., et al, "Removal of Oils from Wastewater Containing Oils," Japan, Kokai, 74, 79,051, July 1974.

33. Giusti, D.M., et al, "Activated Carbon Adsorption of Petrochemicals," Journal Water Pollution Control Federation, Vol. 46, No. 5, May 1974, p. 947.

34. Shelton, T.B.,and J.V. Hunter, "Aerobic Decomposition of Oil Pollutants in Sediments," Journal Water Pollution Control Federation, Vol. 46, No. 9, September 1974.

35. Vorashilova, A.A.,and E.V. Dianova, "Bacterial Oxidation of Oils and Its Migration in Natural Waters," Mikrobiologiya, 15, 3, 1950.

36. Brown, L.R., "The Decomposition of Petroleum Products in Our Natural Water," Report to the Office of Water Resources Research, Department of the Interior, United States Government Printing Office, Washington, D.C., 1969.

37. Blumer, M., et al, "Hydrocarbon Pollution of Edible Shellfish by an Oil Spill," Marine Biology 5, 1970.

38. Shelton, T.B.,and J.V. Hunter, "Anaerobic Decomposition of Oil in Bottom Sediments," Journal Water Pollution Control Federation, Vol. 47, No. 9, September 1975, p 2256.

39. Anon., "Final Environmental Statement for Maintenance Dredging at Sabine-Neches Waterway, Texas," U.S. Army Corps of Engineers, Galveston District, November 1975.

40. Anon., "Final Environmental Statement for Maintenance Dredging at Texas City," U.S. Army Corps of Engineers, Galveston District, September 1974.

41. Anon., "Final Environmental Statement for Maintenance Dredging at Houston Ship Channel," U.S. Army Corps of Engineers, Galveston District, September 1975.

42. Anon., "Draft, Environmental Statement for Harbor Improvement at Brunswick Harbor, Georgia," U.S. Army Corps of Engineers, Savannah, Georgia District, August 1975.

43. Anon., Standard Methods for the Examination of Water and Wastewater, 13th Edition, prepared and published jointly by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation, 1971.

APPENDIX A: SAMPLING AND LABORATORY PROCEDURES

Sampling Procedures

Apparatus

1. Sample Containers. One litre, wide-mouth, square glass bottles fitted with either aluminum, tin, or Teflon-lined screw caps. Note: plastic bottles or caps lined with polyethylene or waxed paper are not to be used as they are a source of contamination.

2. Sample Bottle Cleaning. New bottles shall be used in this service and discarded afterwards. They are to be cleaned by rinsing them out several times with freon and allowed to drain dry by inverting them. It is permissible to dry them by directing a gentle stream of nitrogen into them. Under no circumstances should compressed air be used, as contamination by compressor oil may occur. The bottle caps should also be cleaned in the same manner and replaced on the cleaned bottles.

Reagents

3. Bottle Cleaning Solvent. Freon (1,1,2 Trichlorotrifluoroethane).

4. Sample Preservative. Sulfuric acid, 1:1 aqueous solution. This shall be prepared by cautiously adding a measured amount of concentrated sulfuric acid to an equal volume of distilled water.

Precautions to be Observed while Taking Samples

5. When removing the caps, avoid touching either the necks or the inside tops of the bottles with the hands. Do not rinse the bottle with the sample before filling as oil buildup will occur on the walls. Do not fill the bottle to more than 3/4 of its capacity. If accidently overfilled, the bottle must be immediately discarded and a new one used. It is not permissible to pour out the excess and then analyze the remainder. Bottles must never be reused in this service.

Sample Preservation

6. As soon as possible after samples have been taken, add 5 ml of the sulfuric acid solution to each bottle, replace the caps, and shake thoroughly.

Laboratory Procedures

7. The laboratory procedures used in this study are described in the references listed in Table A-1. Procedures that cannot be found in the material referenced in Table A-1 are described in the remaining sections of this appendix.

Total recoverable oil and grease
and nonpolar hydrocabons,
separatory funnel extraction

8. Scope and application. This method is for the measurement of freon extractable total oil and grease and nonpolar hydrocarbons from surface and saline waters, and industrial and domestic wastes. The gravimetric technique is appropriate when concentration levels are known to be above 10 mg/l and no volatile hydrocarbons are suspected in the sample.

9. Summary of method. The sample is acidified to a low pH (lower than 2) and serially extracted with freon in a separatory funnel. Total oil and grease are measured gravimetrically following evaporation of the freon. The extracted grease and oil are then redissolved in freon. Interferences to the nonpolar hydrocarbon analysis are removed with silica gel adsorbent. The freon is evaporated and the residue is weighed to measure the extracted hydrocarbons.

10. Definitions. Both of the parameters - oil and grease and nonpolar hydrocarbons - are defined by the analytical methods used for their detection. The measurement may be subject to interferences and the results should be evaluated accordingly. Oil and grease is a measure of biodegradable animal greases and vegetable oils along with the relatively nonbiodegradable mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease from all sources.

11. Sampling and storage. A representative sample of 1-litre volume should be collected in a glass bottle. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. The entire sample is consumed by this test; no other analyses may be performed using aliquots of the sample. A delay between

Table A-1

Laboratory Procedures

Analysis or Procedure	Reference Number*
Oil and grease in water, total recoverable, soxhlet extraction	1 (page 226)
Total recoverable oil and grease and nonpolar hydrocarbons, separatory funnel extraction	The procedure is presented beginning on the preceding page; it is taken in part from Reference 1 (page 229) and Reference 2 (page 515)
Oil and grease in sediments, total recoverable	3 (page 412)
Total residue	3 (page 288)
Total suspended solids (TSS)	3 (page 537
Percent solids in sediment	3 (page 539)
Modified standard elutriate test	Identical to the standard elutriate test (Reference 4) except that the filtration step is omitted; the procedure is presented in the following pages
pH Conductivity Temperature Dissolved oxygen	These measurements were made at the sampling site with an instrument (made by MARTEK) capable of in situ analyses
Porosity (total porosity of dried sample calculated from density measurements)	5 (page 300)
Particle-size analysis (hydrometer method)	5 (page 562)

* See reference list at the end of Appendix A and indicated page number in that reference.

sampling and analysis of greater than 4 hr requires sample preservation by the addition of 5 ml of sulfuric acid or hydrochloric acid. A delay of greater than 48 hr also requires refrigeration for sample preservation.

12. Apparatus. Separatory funnel, 1- or 2-litre volume, with Teflon stopcock; filter paper, Whatman No. 40, 11 cm. For gravimetric analysis: flask, boiling, 125 ml (Corning No. 4100 or equivalent), predried at 103°C and stored in a desiccator. Water bath, 70°C. Vacuum pump or other source of vacuum.

13. Reagents. Sulfuric acid, 1:1. Mix equal volumes of concentrated sulfuric acid and distilled water. Concentrated hydrochloric acid may be substituted directly for concentrated sulfuric acid for this reagent. Freon: 1,1,2-Trichlorotrifluoroethane. Sodium sulfate, anhydrous crystal. Silica gel, 60-200 mesh, Davidson Grade 950 or equivalent.

14. Extraction. If the sample was not acidified at the time of collection, add 5 ml sulfuric or hydrochloric acid to the sample bottle. After mixing the sample, check the pH by touching pH sensitive paper to the cap to ensure that the pH is 2 or lower. Add more acid if necessary. Pour the sample into a separatory funnel. Add 30 ml freon to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 min. Allow layers to separate. Filter the solvent layer through a funnel containing solvent-moistened filter paper into a tared 125-ml Erlenmeyer flask for the gravimetric determination. Note: An emulsion that fails to dissipate can be broken either by centrifuging the emulsion or by pouring about 1 g sodium sulfate into the filter paper cone and draining the emulsion through the salt. Additional 1-g portions can be added to the cone as required. Repeat the rinsing of the sample bottle and the filtering of the solvent steps twice more with 30-ml portions of fresh solvent, combining all solvent into the receiving flask. Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5-10 ml freon and collect the rinsings in the receiving flask.

15. Gravimetric measurement. Evaporate the solvent in a water bath at 70°C. Dry on a steam bath for 15 min. Draw air through the flask by means of an applied vacuum for 1 min. Cool in a dessicator for 30 min and weigh (total gain in weight of tared flask = A). Redissolve the extracted oil and grease in freon. Decant into a 125-ml Erlenmeyer flask, rinse with four 10-ml portions of freon, and bring volume up to 100 ml. Add 3 g silica gel. Stopper flask and stir on a magnetic stirrer for 5 min. Filter the solution into a tared 125-ml Erlenmeyer flask. Evaporate the solvent in a water bath at 70°C. Dry on a steam bath for 15 min. Draw air through the flask by means of an applied vacuum for 1 min. Cool in a dessicator for 30 min and weigh (total gain in weight of tared flask = B).

16. Calculations.

$$\text{mg/l total oil and grease} = [(A-C)(1{,}000)]/[V]$$

$$\text{mg/l nonpolar hydrocarbons} = [(B-C)(1{,}000)]/[V]$$

where

A, B = total gain in weight of a tared flask (mg),
C = calculated residue from a freon blank (mg), and
V = volume of sample (ml).

Modified standard elutriate test

17. Summary of test. The elutriate test is a simplified simulation of the dredging process wherein controlled amounts of dredging site water and sediment are mixed together. After centrifugation of the mixture, the resultant elutriate is analyzed for chemical constituents.

18. Apparatus. Laboratory shaker capable of shaking two-litre flasks at about 100 excursions per minute. Box-type or wrist action shakers are adequate. Several one-litre graduated cylinders. Two large (15 cm) powder funnels. Several two-litre large-mouth graduated Erlenmeyer flasks. Note: Prior to use, all glassware and filtration equipment

is washed with a 5 to 10 percent hydrochloric acid solution and then rinsed thoroughly with deionized water. Centrifuge capable of handling six one-litre or 0.5-litre centrifuge bottles at 3,000 to 4,000 rpm. International Model K or Sorval Super Speed are adequate. Glass jars, wide-mouth, one-gallon (3.79-litre) capacity with Teflon liners, and screw top lids should be used for sample containers when analyzing for trace organics. Note: It may be necessary to purchase jars and Teflon sheets separately, in which case the Teflon lid liners may be prepared by the laboratory personnel.

19. Sample collection and preservation. Collect about 3 litres of representative dredge site water samples and place in glass bottles and immediately add 5 ml sulfuric acid. Collection should be made with an appropriate noncontaminating water sampling device. Collect about 2 litres of sediment to be dredged and place in glass bottle. The sediment samples should be taken with a grab sampler in such a manner as to ensure their having the characteristics representative of sediment at the proposed dredging site. The samples should be placed immediately in air-tight containers and filled completely to avoid trapping any air. The period of storage for both should be minimized to prevent changes in the characteristics of the water and sediments.

20. Procedure. Subsample a minimum volume of 1 litre each of the dredge site water. If it is known in advance that a large number of measurements are to be performed, a larger subsample may be warranted. Subsample about a 300-ml sample of sediment from a well-mixed original sample. Mix the sediment and unfiltered dredge site water in a volumetric 1:4 ratio of sediment:water (at room temperature, 22°C, plus or minus 2°C). Example: This is best done by the method of volumetric displacement. One hundred ml of unfiltered dredge site water is placed into a graduated Erlenmeyer flask. Sediment is carefully added via a powder funnel to achieve a resultant volume of 300 ml (a 200-ml volume of sediment will now be in the flask). The flask is filled to the 1,000-ml mark with unfiltered dredge site water, giving a final ratio of 1:4, sediment:water. Cap tightly with a noncontaminating stopper and shake vigorously on an automatic shaker at about 100 excursions per minute for

30 min. A "Polyfilm" covered rubber stopper is acceptable for minimum contamination. After shaking, the stoppered suspension is allowed to settle for one hr. After settling, the supernatant is carefully decanted into appropriate centrifuge bottles and centrifuged to give a clear final solution (the <u>elutriate</u>). Analyze for oil and grease by the separatory funnel extraction method contained in Reference 1. If it appears that the total volume required for all measurements is greater than one litre, proportionately larger volumes of dredged material and dredge site water may be used. Alternatively, several dredged material dredge site water samples may be prepared, following the above procedure in which case the standard elutriates should be combined. Triplicate subsamples should be analyzed by this procedure and the concentration average of the three replicates reported.

1. Anon., "Methods for Chemical Analysis of Water and Wastes," U.S. EPA, Washington, D.C., 1974.

2. Anon., Standard Methods for the Examination of Water and Wastewater, 14th Edition, prepared and published jointly by the American Public Health Association, the American Water Works Association, and the Pollution Control Federation, 1975.

3. Anon., Standard Methods for the Examination of Water and Wastewater, 13th Edition, prepared and published jointly by the American Public Health Association, the American Water Works Association, and the Pollution Control Federation, 1971.

4. Keeley, J.W., and R.M. Engler, Miscellaneous Paper D-74-14, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

5. Black, E.A., Editor, "Methods of Soil Analysis," Part I, American Society of Agronomy, Inc., Madison, Wisconsin, 1965.

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Engineering-Science, Inc.
An evaluation of oil and grease contamination associated with dredged material containment areas / by Engineering-Science, Inc., Austin, Texas. Vicksburg, Miss. : U. S. *Waterways Experiment Station ; Springfield, Va. : available* from National Technical Information Service, 1977.
139, 8 p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; D-77-25)
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